PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C02F 3/10, C08G 18/48

A1

(11) International Publication Number: WO 92/06043

(43) International Publication Date: 16 April 1992 (16.04.92)

(21) International Application Number: PCT/US91/07436

(22) International Filing Date: 8 October 1991 (08.10.91)

(30) Priority data:
594,503 9 October 1990 (09.10.90) US

(71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).

(72) Inventors: LUPTON, F., Stephen ; 1211 Monroe Street, Evanston, IL 60202 (US). SURGI, Marion, Rene ; 1808 Greenleaf Street, Evanston, IL 60202 (US). SHERIDAN, William, G. ; 22 West 530 Birchwood Drive, Glen Ellen, IL 60137-7306 (US).

(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962 (US).

(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS FOR REMOVAL OF ORGANIC POLLUTANTS FROM WASTE WATER

(57) Abstract

A porous biomass support system in a bioreactor affords biodegradation of phenolic materials to a level under 20 parts per billion at a hydraulic residence time of about 15 hours with significantly less sludge formation currently possible by available methods. The porous biomass support system comprises a hydrophilic polymer, preferably polyurethane foam, small particles of activated carbon and suitable microorganisms, which are entrapped with the polymer material. The carbon is self-regenerative and does not have to be periodically replaced or replenished. The entire porous biomass support system can operate for extended periods of time without replacement.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland			SN	Senegal
CI	Côte d'Ivoire	KR	Republic of Korea	SU+	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
CS	Czechoslovakia	LK	Sri Lanka	TG	Togo
DE*	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		

+ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

PROCESS FOR REMOVAL OF ORGANIC POLLUTANTS FROM WASTE WATER

RELATED APPLICATIONS

This application is a continuation-in-part application of United States Patent Application Serial No. 335,610, filed April 10, 1989.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for the removal of organic pollutants from waste water. More particularly, this invention relates to a process for removal of such pollutants especially substituted and unsubstituted phenols by aerobic biodegration using a porous biomass support system in a bioreactor, specifically a fixed bed bioreactor

2. Prior Art

One of the hallmarks of contemporary civilization is that each increment of technological progress almost invariably is accompanied by a similar increment of environmental regress. As the pace of technological advances quickens, so does the march of environmental deterioration. The realization of environmental damage has occurred only relatively recently, so that present society sometimes finds itself burdened with the accumulated sins of the not-too-distant past. But another hallmark of current society is its acceptance of the undesirability of environmental degradation coupled with a determination to minimize and even reverse it wherever possible. Although the return of ground waters to their pristine condition of an earlier era is not a realistic goal,

there is a genuine determination to make our waters as pure as possible. Environmental agencies have set limits for many common industrial pollutants, and as methods of pollution reduction have become more successful in reducing or removing pollutants from waste water, environmental regulations have become more stringent, resulting in an ever tightening spiral whose goal is to reduce pollutants in waste water to that minimum which is technologically feasible.

Among the methods employed to reduce or remove pollutants, bioremediation constitutes an effective and highly desirable approach. Quite broadly in bioremediation pollutants serve as a good source, generally as a source of carbon and/or nitrogen, for microorganisms. Bacterial metabolism converts the pollutants to metabolites generally with a simple chemical structure, sometimes degrading the pollutants completely to carbon dioxide and water in an aerobic process, or to methane in an anaerobic process. But in any event, the metabolites usually have no adverse environmental effects.

Various bioremediation processes are known. For example, U.S. Patent No. 4,634,672 describes biologically active compositions for purifying waste water and air which comprises a polyurethane hydrogel containing (i) surface active coal having a specific surface according to BET of above 50 m^2/g, a polymer having cationic groups and cells having enzymatic activity and being capable of growth. U.S. Patent No. 4,681,852 describes a process for biological purification of waste water and/or air by contacting the water or air with the biologically active composition of U.S. Patent No. 4,634,672. The experimental examples of these patents indicate that the process is not effective for reducing contaminant concentrations in the effluent strain to less than 44 parts per million (ppm). This is not acceptable since

the Environmental Protection Agency (EPA) in some instances has mandated that concentration for some contaminants (such as phenol) in the effluent stream must be as low as 20 parts-per-billion (ppb). (See Environmental Protection Agency 40 CFR Parts 414 and 416. Organic Chemicals and Plastics and Synthetic Fibers Category Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards. Federal Register, Vol. 52, No. 214, Thursday, Nov. 5, 1989. Rules & Regulations, 42522.

Both U.S. Patent Nos. 3,904,518 and 4,069,148 describe the addition of activated carbon or Fuller's earth to a suspension of biologically active solids (activated sludge) in waste water as an aid in phenol removal. The absorbents presumably act by preventing pollutants toxic to the bacteria from interfering with bacterial metabolic activity. The patentees' approach has matured into the so-called PACT process which has gained commercial acceptance despite its requisites of a long residence time, compious sludge formation with attendant sludge disposal problems, and the need to regenerate and replace spent carbon.

Rehm and coworkers have further refined the use of activated carbon in the aerobic oxidation of phenolic materials by using microorganisms immobilized on granular carbon as a porous biomass support system. Utilizing the propensity of microorganisms to grow on and remain attached to a surface, Rehm used a granular activated carbon support of high surface area (1300 m^2/g) to which cells attached within its macropores and on its surface, as a porous biomass support system in a loop reactor for phenol removal. H.M. Ehrhardt and H.J. Rehm, Appl. Microbiol. Biotechnol., 21, 32-6 (1985). The resulting "immobilized" cells exhibited phenol tolerance up to a level in the feed of about 15 g/L, whereas free cells showed a tolerance not more than 1.5 g/L. It was

postulated that the activiated carbon operated like a "buffer and depot" in protecting the immobilized microorganisms by absorbing toxic phenol concentrations and setting low guantities of the absorbed phenol free for gradual biodegradation. This work was somewhat refined using a mixed culture immobilized on activiated carbon [A. Morsen and H.J. Rehm, Appl. Microbiol. Biotechnol., 26, 283-8 (1987] where the investigators noted that a considerable amount of microorganisms had "grown out" into the aquenous medium, i.e., there was substantial sludge formation in their system.

Suidan and coworkers have done considerable research on the analogous anaerobic degradation of phenol using a packed bed of micoorganisms attached to granular carbon [Y.T. Wang, M.T. Suidan and B.E. Rittman, Journal Water Pollut. Control Fed., 58 227-33 (1986)]. For example, using granular activated carbon of 16 x 20 mesh as a support medium for microorganisms in an expanded bed configuration, and with feed containing from 358-1432 mg phenol/L, effluent phenol levels of about 0 06 mg/L (60 ppb) were obtained at a hydraulic residence time (HRT) of about 24 hours. Somewhat later, a beri-saddle-packed bed and expanded bed granular activated carbon anaerobic reactor in series were used to show a high conversion of COD to methane, virtually all of which occurred in the expanded bed reactor; P.FOx, M.T. Suidan, and J.T. Pfeffer, ibid., 60, 86-92 (1988. The refractory nature of ortho- and meta-cresols toward degradation also was noted.

Givens and Sack, 42nd Purdue University Industrial Waste Conference Proceedings, pp. 93-102 (1987), performed an extensive evaluation of a carbon impregnated open-celled polyurethane foam as a microbial support system for the aerobic removal of pollutants, including phenol. Porous polyurethane

foam internally impregnated with activated carbon and having microorganisms attached externally was used in an activated sludge reactor, analogous to the Captor and Linpor processes which differ only in the absence of foam-entrapped carbon. The process was attended by substantial sludge formation and without any beneficial effect of carbon.

The Captor process itself utilizes porous polyurethane foam pads to provide a large external surface for microbial growth in an aeration tank for biological waste water treatment. The work described above is the Captor process modified by the presence of carbon entrapped within the foam. A two-year pilot plant evaluation of the Captor process itself showed substantial sludge formation with significantly lower microbial density than had been claimed. J.A. Heidman, R.C. Brenner and H.J. Shah, J. of Environmental Engineering, 114, 1077-96 (1988). A point to be noted, as will be revisited below, is that the Captor process is essentially an aerated sludge reactor where the pads are retained in an aeration tank by screens in the effluent line. Excess sludge needs to be continually removed by removing a portion of the pads via a conveyor and passing the pads through pressure rollers to squeeze out the solids.

H. Bettmann and H.J. Rehm, Appl. Microbial. Biotechnol., 22, 389-393 (1985) have employed a fluidized bed bioreactor for the successful continuous aerobic degradation of phenol at a hydraulic residence time of about 15 hours using Pseudomonas putida entrapped in a polyacrylamide-hydrazide gel. The use of microorganisms entrapped within polyurethane foams in aerobic oxidation of phenol in shake flasks also has been reported; A.M. Anselmo et al., Biotechnoology B.L., 7, 889-894 (1985).

Known bioremediation processes suffer from a number or inherent advantages. For example, a major

result of increased use of such processes is an ever increasing quantity of sludge, which presents a serious disposal problem of increasingly restrictive policies on dumping or spreading untreated sludge on land and at sea. G. Michael Alsop and Richard A. Conroy, "Improved Thermal Sludge Conditioning by Treatment With Acids and Bases", Journal WPCF, Vol. 54, No. 2 (1982), T. Calcutt and R. Frost, "Sludge Processing - Chances for Tomorrow", Journal of the Institute of Water Pollution Control, Vol 86, No. 2 (1987) and "The Municipal Waste Landfill Crisis and A Response of New Technology", Prepared by United States Building Corporation, P.O. Box 49704, Los Angles, CA 90049 (November 22, 1988). The cost of sludge disposal today may be several fold greater than the sum of other operating costs of waste water treatment.

Use of anaerobic sewage treatment systems has been offered as a solution to the sludge problem. William J. Jewwll "Anaerobic Sewage Treatment", Environ. Sci. Technol. Vol 21, No. 1 (1987). The largest difference between aerobic and anaerobic systems is in cellular yield. More than half of the substrate removal by aerobic systems can yield new microbial mass or sludge, the yield under anaerobic conditions is usually less that 15% of the organic substances removed. However, anaerobic systems are limited in the number of substrate that they can degrade or metabolize such as non-substituted aromatics (See N.S. Battersby & V. Wilson. "Survey of the anaerobic bidegradation Potential of Organic Chemicals in Digesting Sludge." Applied & Environmental Microbiology, 55(2): p. 433-439, Feb. 1989. This is a significant disadvantage in that most industrial processes such as coke production and coal tar processing normally produce non-substituted aromatics as by-products (See J.M. Thomas, M.D. Lee, M.J. Scott and C.H. Ward, "Microbial Ecology of the

Subsurface at an Abandoned Creosote Waste Site." Journal of Industrial Microbiology, Vol. 4, p. 109-120, 1989.

Another disadvantage inherent in some known bioremediation processes is that these processes do not reduce the levels of organic pollutants to reasonable levels [preferable less than about 0.1 parts permillion (ppm)] at reasonable residence times (preferably less than about 24 hours). For example, in the process of U.S. Patent Nos. 5,681,851 and 4,634,672 (See the specific examples), the concentration of phenol contaminants was not reduced below about 44 ppm.

An industrially desirable method of removing phenolic materials from waste waters have the following characteristics. The method would be 1) an aerobic oxidation achieving 2) effluent phenol levels less than 0.1 parts per million (ppm) at 3) hydraulic residence times under 24 hours requiring 4) no activated carbon regeneration or replacement and with 5) substantially less sludge formation than obtained from currently available technology. None of the aforementioned art achieved all of the above, nor does the art give any indication how such a goal can be achieved. We have found that if a specific powdered activated carbon and phenol-degrading aerobic microorganisms are employed in a open-celled hydrophilic polyurethane foam, which is then used as a porous biomass support system in a fixed bed reactor, each of the foregoing goals are readily attained. Levels of effluent phenol down to at least 20 parts per billion can be attained at an HRT of under about 16 hours. Carbon is not physically lost from the reactor, thus avoiding the need for replacement, and is self-regenerative within the reactor. Sludge formation is minimal; comparative tests with other fixed bed reactors show that our immobilized cell

bioreactor (ICB) produces less than 25 percent the amount of sludge formed by presently commercially viable systems. In short, as measured by its performance characteristics, our invention is a a marked improvement over the prior art; relative to the prior art, our invention represents a difference in kind rather than a difference in degree.

Reduced sludge formation attending our process is neither an incidental nor a minor benefit. A major result of increased wastewater treatment is a never increasing restrictive policies on dumping or spreading untreated sludge on land and at sea. The cost of sludge disposal today may be several fold greater than the sum of other operating costs of wastewater treatment. Accordingly, the reduction in sludge levels characteristic of our invention has immediate, substantial economic benefit and alleviates the pressures of sludge dumping.

THE SUMMARY OF INVENTION

This invention relates to materials for porous biomass support system (PBSS) and processes for biological treatment of waste streams, specifically biodegration of organic and waste streams.

DESCRIPTION OF THE DRAWINGS

Figure 1 is an adsoption curve measuring phenol adsorbed for hydrophilic and hydropholic foams and the foams impregnated with carbon.

Figure 2 is an adsorption curve measuring phenol adsorbed for a hydrophilic foam and a carbon impreganted hydrophilic foam.

Figure 3 is an adsorption curve for hydrophobic foam and carbon impregnated hydrophobic foam.

Figure 4a is a 1-pulse $C-^{13}$ (labelled) phenol NMR 1-pulse and cross polarization/magic angle spinning of carbon impregnated hydrophilic foam after adsorption

of phenol.

Figure 4b depicts a C-^{13} NMR of carbon impregnated hydrophilic foam after exposure to phenol using cross-polarization of magic angle spinning (CPMAS).

Figure 5a is a CPMAS C-^{13} NMR of a hydrophilic foam.

Figure 5b is a CPMAS C-^{13} NMR if a hydrophobic foam.

Figure 6 is a 1-pulse MAS C-^{13} NMR of carbon impreganted hydrophilic foam and carbon impregnated hydrophobic foam after exposure phenol.

Figure 7 is a schematic drawing summarizing the NMR results on phenol adsorption of a carbon impreganted hydrophilic foam.

Figure 8 depicts the response of bioreactors containing polyurethane foam (PUF) supports to schock loads of phenol.

Figure 9 depicts the total phenolic removal by reactors having varied polyurethane foam supports.

Figure 10 depicts the removal of aromatic pollutants by two bioreactors; one having a carbon impreganted hydrophilic foam support and an unimpregnatedd hydrophilic polyurethane support.

Figure 11 is a scanning electron micrograph of carbon impregnated foam (Hypol) when activated carbon is introduced during polymerization.

Figure 12 is a scanning electron micrograph of a foam (Hypol) when the carbon is surface impregnated by solvent swelling the foam using ethyl acetate.

DETAILED DESCRIPTION OF THE INVENTION

Much of the work to date in biomediation relates to the use of polyurethane foams in treatment process. This invention focuses on improved biomass support materials, which include polyurethanes, as well as their use as biomass support systems in

bioreactors.

One aspect of this invention relates to discovery that certain polymers can adsorb phenolic pullutants; however, the adsorption of these compounds to polymers can depend greatly upon the composition of the various polymers. In addition, we have discovered that the absorption characteristics of a polymer can be very varied by the presence of absence of activated carbon.

One embodiment of the present invention relates to a biomass support comprising a hydrophilic polymer and activated carbon. In general, these polymers provide a porous biomass support for microorganisms. In preferred embodiments, the polymer is hydrophilic polyurethane foam. Polyurethane foams of the preferred embodiments of this invention can be formed directly from the reaction of di-and/or polyfunctional isocyanate compounds in the polymer along with appropriate catalyst or by a partial reaction of the di-and/or polyfunctional isocyanate compounds with the polyol to form a NCO polyurethane prepolymer. Preferably, the NCO polyurethane prepolymer possesses 3 to 10% of the isocyanate compounds as free NCO groups. Therein, water can be used to catalyze the cross reaction of the remaiming groups to form the urethane foam. The adsorption and/or absorption of organic polutents, e.g. phenol, onto and into the polyurethane foam can be affected by both the type of polyol used as well as the portion of cross-linked isocyanate compounds present in the foam. It is preferred to limit the amount of aromatic groups, specifically aromatic isocyanate compounds, in the hydrophilic polyurethane foam in order to maintain the hydrophilic characteristic of the polymer. Preferably, the hydrophilic polymer contains less than about 30% by weight of aromatic isocyanate. In further preferred embodiments of the invention, the

hydrophilic polymer has at least 90% by weight of polyethylene oxide and at least less than about 25% by weight of aromatic isocyanate. In particular preferred embodiments, the polyol content of hydrophilic polymer is at least 95% by weight polyethylene oxide and less than about 20% of aromatic isocyanate. In the more particularly preferred embodiments of invention, the polyol content is greater then about 99% by weight polyethylene oxide and less than about 15% by weight of aromatic isocyanate. The hydrophilic polymers described above are combined with activated carbon. The activated carbon used is generally in powder form. Preferably, the carbon is added either to the polyol prior to the cross linking reaction with isocyanate or with the NCO prepolymer prior to reaction with water. The carbon may also be applied to the foam by mixing carbon in the foam in the presence of a binder which adheres the carbon to the foam. Such a binder would be selected so as to not inactivate the carbon once the carbon is applied.

The hydrophilic polymer supports for use in the bioremediation are combined with activated carbon since the activated carbon can enhance the adsorptive capacity of a polymer, e.g. polyurethane foam, for organic polutents, which include aromatic pollutants, such as phenol. Carbon concentrates the pollutants. Although carbon can be added to hydrophilic polymers and hydrophilic polymers, only when carbon is combined with the hydrophilic polymers is phenol absorbed and in a mobile state. Once absorbed in a mobile state, the phenol is able to interact with carbon. It is discovered that carbon is not in a "mobile state" when combined with a hydrophilic polymer, for example polyurethane hydropholic polyurethane foam.

As shown in Table A, hydrophobic foam and hydrophilic foam each with 20% powdered activated

carbon have a high adsorption coefficient (i.e. large capacity to adsorb phenol); however, the Langmuir adsorption curves and carbon C^{-13} phenol/NMR binding studies summarized at Table 2 and Figures 1 through 7 show that the carbon present in the hydrophilic foam is able to interact with and in fact absorb and adsorb phenol while embedded in the foam matrix. On the contrary, this is not a case with conventional hydrophobic foams. When carbon is embedded in the hydrophibic foam it has a high capacity to absorb the phenol without the presence of activated carbon. The hydrophilic foams, on the other hand, do not have a high capacity to adsorb phenol without the addition of an appropriate carbon. The adsorption of C^{-13} phenol to carbon impregnated carbon impregnated hydrophilic and hydrophobic foams was followed using Magic Angle Spinning/Cross Polarization NMR Spectroscopy. The results are shown in Figure 4. Peak A at Fig. 4A represents the phenol that is absorbed into hydrophilic foam. Phenol shows a "fluid" NMR signal indicating that it is, in fact, mobile within the polyurethane, which appears to the phenol molecules as a viscous liquid. Peak B represents the phenol which adsorbed to the PAC. This phenol appears as a solid in the NMR and is held tightly by the carbon. Peak C represents phenol that is adsorbed onto the hydrophibic phenol. This phenol has a solid signal in the NMR rather then the liquid signal that was associated with the phenol in the hydrophilic phenol. There is no phenol signal associated with the activated carbon that is present in the hydrophobic foam although the amount of phenol that adsorbs to the hydrophobic foam is relatively high compared to that absorbed into the hydrophilic foam. A summary of the results obtained by these studies is depicted at Figure 7.

The above results indicate that the hydrophilic

foam behaves as a viscous liquid permitting phenol to diffuse through the foam to the carbon support. It is believed that the "viscous" characteristic is provided by the long chain polymers unit of the hydrophilic foam having limited amounts of rigid aromatic (crystalline) region, but large amounts of sp3 carbon oxygen units due to the polyols. The motions of the long chains (of polyols) are sufficiently rigid to permit the existance of free volume and promote the migration of phenol from one free volume unit to the other (See Figure 4A). Because of the mobile phenol and viscous polyurethane foam, the phenol is adsorbed by the polymer and diffuses to the carbon throughout the foam, wherein the phenol is exposed to microorganisms present throughout the foam.

In order to maximize the benefit of activated carbon in a porous biomass support system, the carbon employed should have an effective affinity for aromatics, specifically phenols. The affinity of the carbon is measured by adsorption of phenol and whether it follows the Langmuir absorption curve. An effective carbon follows the Langmuir adsorption curve. The Langmuir curve describes the adsorption of adsorbents as a monolayer into the absorbent. This can be described mathematically as;

$$Q = \frac{CN}{C + K_d}$$

where:

Q is the amount of phenol per unit of adsorbent.

C is the phenol concentration in solution at equilibrium conditions.

N is the maximum adsorbable amount of phenol at saturation conditions.

K_d is the equilibrium phenol concentration when Q = N/2.

The values of N and K_d can be determined from a plot of C/Q versus C thus:

$$C/Q = C/N + K_d/N$$

where:

the X intercept + $-K_d$

the Y intercept + K_d/N

the K_d value reflects the carbon infinity for phenol. The carbon selected should exhibit a K_d value of at least about 0.001 mg/L. Preferably the K_d value ranges from about .001 to 300 about mg/L. More preferably the K_d value ranges from about 10 to about 150 mg/L. In particularly preferred embodiments, the K_d ranges from about 10 to about 100 mg/L. It is important to optimize the K_d value since the infinity of microorganism phenol, generally indicates as K_s, will generally be less then about 300 gm/L.

In order to optimize interaction between the activated carbon and the biodegradative microorganisms, the K_d of the carbon need to be slightly higher than the K_s of the micro-organism. If the K_d of the carbon is well below that of the micro-organism the carbon will act to tightly bind the

organic substrates from the liquid phase but will not release them at a concentration at which the bacteria will have a high substrate utilization rate. If on the other hand the K_d of the carbon is very large compared to the K_s of the micro-organisms there will be a poor buffering effect on highshock loads of phenol and when the phenol concentration is lower and approaches the K_s of the micro-organisms, the carbon will have a poor ability to concentrate phenol at its surface and thus stimulate microbial growth. An effective range of K_s/K_d ratios is between 1:1 and 1:50. The more preferred range is between 1:1 and 1:20. The most preferred range is between 1:1 and 1:10. Ks values and other biomass parameters are discussed in the following publications which are incorporated herein by references (i) D. Orhon et al., "The Effect of Reactor Hydranlics and the Performance of Activated Sludge Systems - I. The Traditional Modelling Approach" Wat. Res Vol 23, No. 12 pp. 1511 and 1512 (1989), (ii) Ren Der Yan et al., "Dynamic and Steady State Studies of Phenol biodegradation in Pure and Mixed Cultures", Biotechnology and Bioergineering, vol XVII, see pp. 1211-12 (1975) and (iii) Spectra, Jr., "Sensitivity Analysis of Biodegration/Adsorption Models" Journal of Environmental Engineering, Vol. 116, No. 1 see pp. 32-39 (February 1990).

In particular preferred embodiments of the invention, the activated carbon is selected from wood, charcoal and anthracite coal. Wood charcoal is more preferred since it may have an affinity for phenol which approaches the affinity of phenol-degrading microorganisms currently available, allowing maximization of interaction between the phenol and microorganism.

The porous biomass support system (PBSS) is at least about 5% by weight of activated carbon (based on

the total weight of the carbon and polymer support). Preferably, the PBSS is from about 5 to about 85% by weight of activated carbon. More preferably, the PBSS is at least about 10% by of activated carbon. Most preferably, the PBSS is about 20 to about 40% by weight of activated carbon. In addition to activated carbin, inert fillers can be employed in the biomass support; however, our biomass system is operable in the absence or substantially absence of fillers. When employed, the filler material is added prior to forming the open-celled foam support.

The microorganisms which are used in the practice of this invention are aerobic microorganisms selected to degrade the pollutants of interest in ways well known to those in the art. Thus, cultures isolated from the pollutant-containing waste streams themselves usually are enriched and subsequently incorporated into the PBSS. Conventional microorganisms used for degration and methods for their selection are broadly known. The PBSS preferably, is prepared by forming the foam in the presence of a suspension of powdered activated carbon and suitable microorganisms. Thus, for example, a suitable polyurethane foam precursor can be mixed with an aqueous suspension of powdered activated carbon and aerobic pollutant-degraded microorganisms, often in the presence of blowing or foaming agents such as carbon dioxide or surfactants, generally with vigorous mixing at the beginning of polymerization followed by quiescence of permit good void formation. The foam as produced is then cut into an appropriate particle size and loaded into a bioreactor. The pollutant-containing aqueous feed is pumped through the reactor, generally in an up flow configuration. It is important for a reactor to be aerated to provide the necessary oxygen-rich environment for proper microbial metabolism and pollutant degradation. Oxygen generally is

incorporated along with the feed at the bottom of the reactor, when the reactor is run in an up flow configuration, so as to afford an aqueous stream saturated, or nearly saturated, in oxygen. A minimum dissolved oxygen level of at least 2 mg/L is desirable, and an oxygen level of 5 mg/L or higher is preferably.

The porous biomass supported systems of this invention can be used in any bioreactor: a continuous stirred-tank bioreactor (CSTBR), fixed-bed or pinked-bed bioreactor (PBBR) or fluidized-bed reactor (FBBR).

In a preferred embodiment, the porous biomass support system (PBSS) is employed in a fixed bed bioreactor. In such a reactor, the PBSS is an open-celled hydrophilic foam, e.g. polyurethane foam having entrapped within its pores powdered activated carbon and aerobic pollutant-degrading microorganisms. The microorganisms can be added prior to the polymerization or cross-linking of the foam or thereafter. When added after preparation of the foam, the PBSS is treated or "loaded" with microorganism. The PBSS is loaded by adding microorganisms to the reactors packed with the PBSS, optionally along with organic pollutant, and the reactor contianing supports, microorganisms and pollutant are incubated in a batch mode so that a large population of microorganisms develops within the reactor. A small proportion of these microorganisms will attach to the surface of the PBSS. Fresh medium containing organic pollutant then pumped through the reactor. The majority of the unattached microorganisms are removed by the flow of medium through the reactor but the attached microorganisms grow and multiply and in doing so form a firmly attached "bioflim" of microbes and extracellular polymer which entraps more microorganisms within the pores and on the surface of

the PBSS.

The carbon concentrates (as shown by NMR) pollutants on its surface. If the carbon were macroporous with pores of a size to accommodate the microorganisms, and if carbon were of a small particle size with a high surface area, we reasoned that the proximity of microorganisms to the locally high concentration of adsorbed pollutant would result in their faster ad more complete degradation. This would afford lower effluent pollutant levels while "protecting" microorganisms from the toxic effects of pollutants. The "immobilization" of bacteria and carbon within the pores of the foam prevents the physical loss of carbon and tends to minimize sludge formation, that is, growth of the microorganisms into the aqueous feed. The PBSS in a fixed bed reactor then provides the high concentration of biomass permitting a relatively low hydraulic retention time.

Stated somewhat differently, at levels above 1-5 pmm microorganisms utilize phenol rapidly because of the high binding constants between the microorganisms and phenol, but at levels under 1 ppm utilization is slow and phenol utilization is a lengthy process. The carbon in our PBSS concentrates phenol in the vicinity of microorganisms; the local concentration of phenol as seen by the microorganisms is very high, leading to higher rates of phenol utilization.

The porous biomass support system of our invention is unique in the way it combines foam, carbon, and microorganisms. The invention as described more fully within combines the aforementioned porous biomass support system in a fixed bed operation to afford low phenol effluent levels at a low hydraulic residence time and with significantly less sludge formation than previously attainable. The invention thus affords advantages of considerable industrial merit not previously

attainable by currently available systems.

The organic pollutants which may be degraded by the use of our invention include phenolic material as a major class. Members of this class include phenol itself, the cresols, resorcinol, catechol, halogenated phenols such as 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2.4-dichlorophenol, pentachlorophenol, nitrophenols as 2-nitrophenol and 4-nitrophenol and 2, 4 dimethylphenol. Another important class or organic pollutants consists of aromatic hydrocarbons, such as benzene, toluene, the xylenes, ethylbenzene, and so forth. Polynuclear aromatic hydrocarbons are an important subclass as represented by naphthalene, anthracene, chrysene, acenaphthylene, acenaphthene, phenanthrene, fluorene, fluoranthene, naphthacene, and pyrene. More generally, the method within can be applied to streams containing organic pollutants without limitations, so long as they are capable of being degraded by aerobic microorganisms.

The pollutants which are to be biodegraded in the practice of this invention typically are found in aqueous waste streams at industrial manufacturing facilities. For example, phenol is found in waste streams of phenol manufactures, of phenol users as phenol resin producers, of coal tar processing facilities, of wood pulping plants and other facilities practicing delignification. This is not to say that the process can or must be practiced only on such streams. The process which is the invention herein may be practiced on any aqueous feed containing levels of organic pollutants which are to be reduced and which may be greater than that permitted by the environmental protection agency.

The key to our process is the passage of an aqueous feedstock under oxygen rich conditions through a fixed bed reactor of porous biomass support system. The PBSS which is the core of our invention has three

elements; an open-celled hydrophilic foam, powdered activated carbon having an effective affinity for organics entrapped within the foam, and viable, aerobic, pollutant-degrading microorganisms also entrapped within the interior of the foam. Incorporation of powdered activated carbon within the foam prevents its physical loss in fixed bed reactor operation, obviating the need for periodic replacement or replenishment of carbon, and also facilitates its bioregeneration. It is postulated that the entrapment of microorganisms within the foam, especially in close proximity to the powdered activated carbon, is responsible in part for the low sludge formation accompanying the practice of this invention, and also is responsible in part for the low residual levels of pollutants in the effluent, reasons for which have been stated above in the discussion of our working hypothesis of this invention.

The foam used in the practice of this invention is a particulate open-celled foam to accommodate feed flow in the fixed bed configuration. That is, it is important for the pollutant-containing aqueous feed to flow through the interior of the foam. For the same reasons it is desired that the foam has high macroporosity; foam desirably are at least 2 millimeters, and preferably are on the order of 5-6 millimeters in size. The foam also needs to be resistant to the shear forces and abrasion present in a fixed bed reactor, and should have good crush strength. The foam is desirably semiflexible, with a density of under about 2 pounds per cubic foot for optimum economic feasibility. However, higher density foams, of 4-5 pounds per cubic foot or even higher, are usable. It needs to be realized that foam density is related to the economics of the invention and not to its performance; the invention may be practiced with a large range of foam density, even if certain

ranges may present distinct economic advantages.

As noted the foam can be prepared in the presence of a suspension of powdered activated carbon and aerobic, pollutant-degrading microorganisms so as to entrap both of the latter within the interior of the foam. When prepared the PBSS contains at least 5 weight percent, and up to about 85 weight percent, preferably not greater than 50 weight percent, of activated carbon on a dry basis. When activated carbon is present at a level under about 5% its effectiveness is reduced to a point where the resulting PBSS is only marginally advantageous. At levels above about 50 weight percent incoporation of activated carbon the foam becomes fragile, losing its structural integrity and becoming easily physically damaged. Most often the PBSS when prepared contains at least about 10 weight percent activated carbon, and usually contains from about 20 up to about 40 weight percent porous activated carbon.

The powdered activated carbon has a surface areas at least about 500 m^2/g, preferably at least about 700 square meters per gram, and is of a size such that at least 70% of the carbon particles are smaller than about 44 microns, that is, a minimum of 70% pass through a 325 mesh sieve. The powdered activated carbon has as high a pore volume as is practical, at least 0.5 cc/g, typically at least 0.7 cc/g, with as great a porosity as possible contributed maximized the concentration of microorganisms in the immediate proximity of the activated carbon surface. Typical powdered activated carbons used in the practice of this invention have a surface area 700-1000 m^2/g, pore volume 0.7-1o cc/g, with 70-100% of the particles under 44 microns in size. Although these correspond to characteristics of commercially available material, our invention per se imposes no such limitations. In particular, high surface area carbons, even up to

1500-2000 m^2/g, with as high a pore volume as possible are quite desirable for us in our process.

The pollutant-containing aqueous feed with dissolved oxygen then be passed through the fixed bed of the PBSS. An hydraulic residence time of under about 30 hours, generally less than about 24 hours, and usually no more than about 15 hours, suffices to attain an effluent phenol level of under 0.1 parts per million, usually under 20 parts per billion. The particular hydraulic residence time depends upon the amount of phenolic materials in the feedstock, operating temperature, the presence of other materials in the feedstock, operating temperature, the presence of other materials in the feedstock, the density of microorganisms in the fixed bed, and so forth. The low hydraulic residence time is a consequence of both the particular PBSS used and the fixed bed configuration. The low level in the effluent is a consequence of the presence of activated carbon in the particular configuration of the PBSS used. The low sludge level is a consequence of the particular PBSS in a fixed bed configuration.

The pH of the pollutant-containing feed may need to be adjusted for optimum biodegradation. Nutrients, and especially phosphate and ammonium salts, any need to be provided, but sufficient amounts often are present in the aqueous feed to satisfy minimum requirements of the microorganism.

PBSS of our invention can be used over extended periods of time without replacement or maintenance of any type. It is anticipated that in most cases the initial charge may be used for at least one year and up to perhaps five years before replacement becomes necessary. Throughout this time the reactor should operate with significantly less sludge formation than that from currently available systems, affording important advantages in sludge disposal costs. A

comparison of representative levels of sludge production in several biological treatment systems is summarized in the following table, where sludge production is measured per unit reduction of COD (chemical oxygen demand).

SLUDGE PRODUCTION IN BIOLOGICAL TREATMENT SYSTEMS

System	Sludge Production (kg dry wt sludge/metric ton COD consumed)
Aerobic activated sludge	400 - 600 (a)
Anaerobic digester	20 - 150 (a)
Sybron biotower	200 - 300 (b)
This invention	30 - 100 (b)

(a) R.E. Speece, "Anaerobic Biotechnology for Industrial Wastewater Treatment", Environmental Science and Technology, Vol. 17, p416A - 427A, 1987

(b) Experimental results; cf. Example 8

In practice, the method of our invention can reduce phenol levels to under 0.1 ppm, and generally to under 20 ppb, with sludge formation of no more than 100 kg dry weight sludge, often only 30 kg dry weight sludge, per metric ton total chemical oxygen demand consumed.

The following examples are merely illustrations and representative of our invention which is of considerably larger scope. These examples should not be considered limiting in any way.

In the examples and Figures generated therefrom, the materials used for the hydropholic foam is a polyurethane prepolymer (Hypol) having a polyol content greater than 90% (approx. 100%) polyethylene

oxide and an aromatic iso-cyanate contact of less than 15% by weight.

The hydrophobic polyurethane foam (General Foam) has a polyol content of less than 80% by weight (polyol is approximately 50% polyethylene oxide/50% polypropylene oxide and the aromatic isocyanate (toluene disocyanate) content of approximately 25 to 35% Powdered activated carbon is Calgun PAC type WPX.

Example 1: Effective Impregnation of Polyurethane Foams using Powdered Activated Carbon (PAC)

The effectivness of impregnating polyurethane foams with Powdered activated carbon to enhance the adsorptive capacity of the foam for phenolic pollutants was determined for a hydrophilic polyurethane (hypol) with a low degree of TDI cross-linking, a Polyether diol with ethylene oxide content of greater than 90% and a TDI content of less than 15% by weight and a hydrophobic polyurethane (General Foam) with high degree of cross-linking, a polyether diol with ethylene oxide of less than 80% and a TDI content of approx. 25% to 35% by weight.

The powdered activated carbon was blended with the polyol precursor or prepolymer prior to foaming at a concentration of 20%.

The absorption co-efficeint of the polyurethane itself and the polyurethane impregnated with PAC for phenol was determined by the addition of foam block of approx. 3/8 inch cube into a solution of phenol in distilled water. The adsorption co-efficient can then be calculated thus:

$$\text{adsorption coefficient (A)} = \frac{\text{gm phenol remaining/ gm water}}{\text{gm phenol absorbed gm adsorbent}}$$

The adsorption coefficeints of the umimpregnated and impregnated polyurethanes were determined to be:

Table A

Foam Type	Á constant
Hydrophilic Foam	9.0
Hydrophilic Foam with 20% PAC	74.5
Hydrophobic Foam	62.6
Hydrophobic Foam with 20% PAC	84.4

It was unexpectedly found that the hydrophobic foam had a high capacity to adsorb phenol even without the impregnation with PAC. Furthermore the PAC impregnation did not lead to a significantly greater adsorptive capacity for phenol over the non impregnated hydrophobic foam. The Langmuir adsorption curves for the umpregnated and impregnated polyurethane foams were determined to by ploting C/Q versus C to determine N and K_d values for the Langmuir adsorption.

Table B

Hydrophilic		Hydrophilic 20% PAC		Hydrophobic		Hydrophobic 20% PAC	
C	Q	C	Q	C	Q	C	Q
55	0.0006	3	0.0221	62	0.0040	47	0.0050
103	0.0015	16	0.0496	121	0.0080	87	0.0110
288	0.0029	94	0.0885	291	0.0210	200	0.0300
548	0.0058	490	0.1169	615	0.0390	489	0.0510
2192	0.0254	1484	0.1614	1426	0.0570	959	0.1400
3174	0.0411	2526	0.1939	2770	0.1230	1724	0.2280
3884	0.0488	3374	0.2596	3984	0.2020	2967	0.3030

Plots of Q versus C and semi-reciprocal plots of C/Q versus C indicate that only the PAC impregnated hydrophilic polyurethane follows the Langmuir adsorption curve. A number of different carbons were evaluated for Langmuir adsorption of phenol. The following results were obtained:

Table C

Carbon Type	N (gm phenol / gm carbon)	K_d (mg / L)
Germantown Lampblack	weak, non-Langmuir adsorption	-
Bone Char	Weak, non-Langmuir	-
Wood Charcoal	0.2281	90
Anthracite Coal	0.3305	120

Of the four carbons tested only the wood charcoal and the anthracite coal PACs showed Langmuir type adsorption curves for phenol. The adsorption parameters of the hydrophilic polyurethane impregnated with these carbons were determined to be:

Table D

Foam/PAC	N (gm phenol / gm foam/PAC)	K_d (mg / L)
Hydrophilic Foam + 20% Wood Charcoal PAC	0.0266	52
Hydrophilic Foam + 20% Anthracite Coal PAC	0.0383	107

Example: 4 Response of Bioreactors Containing Polyurethane Foam Supports to Shock Loads of Phenol

The following example shows the unexpected superior performance of hydrophilic polyurethane foam impregnated with activated carbon over conventional hydrophobic polyurethane foam and same foam impregnated with activated carbon with regards to shock loading of bioreactors with phenol. The comparison of the foams is shown in the following Table E

Time (days)	Phenol Concentration (ppm)			
	Inlet Wastewater	Hydrophobic PUF	Hydrophobic PUF + PAC	Hydrophilic PUF + PAC
1	105	0.005	0.003	0.013
4	130	0.003	0.002	0.004
5	1100	228	278	113
6	1330	4	18	0.021
7	1210	0.009	0.008	0.005
8	1300	0.008	0.008	0.005
14	1160	0.121	19	0.189

The supports were evaluated in glass columns of dimensions 64 cm height x 3.4 cm diameter. The columns were packed with foam blocks of approximately 1 cm^3 in size. Phenol containing water was pumped into the bottom of the column and exited from the top. Air was sparged from the bottom of the column using a ceramic sparging stone and exited the reactor from the top also. The flow rate of water through the reactors was such that the hydraulic residence time was 12 hours. Phenol levvels in the effluent from the reactors was determined by colorimetric assay.

The results from this study (Fig. 8) showed that the carbon impregnated hydrophilic foam supports enabled the bioreactor to produce an effluent of significantly lower phenol concentration when compared to the bioreactors employing hydrophobic foam or hydrophobic foam impregnated with activated carbon. There was in fact little difference between the reactor with hydrophobic foam only and the reactor containing carbon-impregnated foam.

Example 5: Total Phenolics Removal from Coal Tar ProcessingWastewater using bioreactors with Polyurethane Foam Supports

The following example unexpectedly shows the superior performance of carbon impregnated hydrophilic foam used as a support in bioreactors for the removal of total phenolics foam without carbon. Twenty gallon glass tanks were used as bioreactors. The tanks were filled with foam blocks of approximately 1 cubic inch in size. The packed bed reactor was sparged with air by means of perforated tubing that ran across the bottom of the tanks. Wastewater from a coal tar processing plant, containing a multitude of phenolic and other aromatic pollutants, was fed to the bioreactor as such a rate that the hydraulic residence time was approximately 24 hours. The following results were obtained:

TABLE F

Time (days)	Total Phenolics Concentration (ppm)		
	Inlet Wastewater	Hydrophilic PUF	Hydrophilic PUF + PAC
1	750	4.8	1.5
4	600	25.0	5.0
11	700	6.0	2.4
22	475	5.0	1.2
27	550	6.0	1.6

The results (Fig. 9) show that the bioreactor that employed the carbon impregnated hydrophilic polyurethane supports produced an effluent with a significantly lower level of total phenolics compared to the bioreactor that used hydrophilic foam that was not impregnated with carbon.

The removal of specific aromatic pollutants by the bioreactors was determined using solid phase extraction and GC/MS. The following results were obtained:

TABLE G

Time (days)	Concentration (ppb)					
	Hydrophilic PUF			Hydrophilic PUF + PAC		
	Phenol	2,4-Dimethyl Phenol	Naphthalene	Phenol	2,4-Dimethyl Phenol	Naphthalene
1	14	171	59	20	18	13
4	7,711	590	660	19	98	12
11	43	257	438	13	32	64
22	12	140	81	47	3	2
27	32	165	134	20	3	4

The results (Fig. 10) show that the bioreactor that employs the hydrophilic polyurethane foam impregnated with carbon produces an effluent that is lower in substituted phenol and napthalene as well as phenol compared to the foam without carbon addition.

EXAMPLE 6

Preparation of the Porous Blomass Support System.

A. Preparation of bacterial cluture. To prepare bacterial inoculum adapted to the waste stream that is to be treated, enrichment cultures were set up by adding to samples of the waste stream 100 mg/L ammonium sulfate and 25 mg/L of sodium phosphate

followed by adjustment of pH to 7.0. One hundred mL portions of the foregoing sample were dispensed into 250 mL flasks and inoculated with soil or sludge, then incubated at 25°C on a rotary shaker (250 rpm) for 7 days. At this time 1 mL subcultures were dispensed into new wastewater samples and incubated for another 7 days. Cultures were then maintained under these conditions prior to foam manufacutre.

B. Foam Preparation. The polyurethane used to manufacture the biofoam was a toluene diisocyanate polyether prepolymer supplied by W.R. Grace under the trade name Hypol. Foaming occurs upon reaction with water, and the pore structure of foam can be altered by the addition of surfactants as well as auxiliary blowing agents such as chlorofluorocarbons or exogenuous carbon dioxide to afford interconnected pores of at least 2 millimeter size. The following procedure is typical.

Five gallons (50 lbs) of polyurethane prepolymer (HYPOL 2000) was added to a mixing vessel of approximately 100 gallons capacity. Twenty-five pounds of activated carbon (Calgon PAC type WPX), 2 mL of tween 80 surfactant, and 20 grams of sodium bicarbonate were mixed with the HYPOL 2000 to make a homogenuous prepolymer/carbon/additive mixture using a high torque mechanical mixer. A homogenuous mixture is indicated when the material has a wet "sheen" appearance. Two mL of Tween 80 and 10 mL of glacial acetic acid were added to 5 gals. of bacterial cluture (optical density at 600 nm approx. 0.2). The bacterial culture then was added to the polyurethane prepolymer/carbon mixture in the mixing vessel and mixed rapidly with the high torque mechanical mixer. At first, the mixture was very viscous but rapidly lost its viscosity and was easily mixed. As the degree of crosslinking increased, the material once again began to become viscous. At this stage it is

very important to stop mechanically mixing the solution and allow the foaming to proceed. The sodium bicarbonate and the glacial acetic acid neutralize each other and in the process generate exogenuous carbon dioxide. This extra gas formation added with that generated from the HYPOL crosslinking reactions leads to large and interconnected pores in the biofoam. The presence of the Tween 80 amplifies this effect by decreasing interfacial surface tension and promoting foam formation. The foam was usually alllowed to cure for 10 to 20 minutes before it was cut up into blocks or shredded in a fitzmill comminuting machine to produce biofoam blocks of the desired size. The total volume of biofoam produced from this quantity of prepolymer and bacterial cluture and produced under the above conditions was between 80 and 100 gallons.

EXAMPLE 7

Preparation, Operation, and Performance Characteristics of Fixed Bed Reactors. Four glass reactors were used as fixed bed reactors with different packing material as described in table 1. Fixed bed reactirs using a bed of biofoam of this invention is referred to as an immobilized cell bioreactor (ICB). Each bench scale fixed bed reactor consisted of a glass column of approximately 580 ml total capacity 64 cm high and 3.4 cm internal diameter. The reactor volume occupied by water and foam was approximately 480 ml. The biofoam in the reactors consisted of irregular 3/8" cubic blocks with the bed held in the reactor by means of 1/14" wire mesh screens 53 cm apart. Biofoam volume in the reactor was approximately 350 ml with an internal void volume of 260 ml. The interstitial water volume between the biofoam blocks was approximately 130 ml. Reactors were operated in a cocurrent upflow mode,

i.e., both air and water flowing from the bottom to the top of the reactor, unless otherwise indicated. Compressed air (40 psig) was used to aerate the column throug a sintered glass sparger located at the bottom of the column. A gas regulator was used to regulate the aeration rate through the sparger at a level between 4 and 12 L/hr. Wastewater was pumped from a 4 liter feed reservoir to the bottom of the reactor with a Masterflex peristaltic pump. Typical wastewater flows through the reactor ranged from 0.25 to 0.8 ml/min. The effluent from the columns was collected in another 4 liter reservoir. Both the feed and effluent reservoirs were placed in ice baths. The ambient temperature of the columns was approximately 25°C.

TABLE 1

Reactor	Packing/Catalyst	Flowpath
#1	Polypropylene discs, cells allowed to colonize surface (natural biofilm developed).	Upflow
#2	P-1 cells[a] entrapped in polyurethane foam (5g of HYPOL 3000 with 100 mL of P-1 culture	Upflow
#3	P-1 in foam with activated carbon (5g of HYPOL 3000, 25g of ATOCHEM 830 DC[b] and 100 mL of P-1 culture).	Upflow
#4	P-1 in foam with activated carbon as for #3.	Downflow

a. Yeast cells enriched as described in Example 1 from hydrocarbon contaminated soil sample from Des Plaines, IL.

b. Powdered activated carbon from Atochem Co.

In each case the feed consisted of an aqueous solution containing 0.1 g/L dibasic potassium phosphate, 0.5 g/L ammonium sulfate, 0.1 g/L magnesium sulfate, 0.05 g/L calcium chloride, 0.01 g/L yeast extract, and 500 mg/L phenol. The phenol present in the effluent from the columns was analyzed by solid phase extraction with cyclohexyl columns supplied by Analytichem Co. by the 4-aminoantipyrine assay (R.D. Yang and A.E. Humphrey, Biotech. and Bioeng., 17, 1211-35 (1975)). Suspended solids in the reactor effluents were determined by measuring the optical density at 600 nm. The columns were operated at a liquid hourly space velocity between 0.03 and 0.12 hrs^{-1} for a total period of 116 days at an aeration rate (air introduced at bottom of reactor of 12 liters per hour and an average temperature of 25°C. Results are tabulated in the following tables.

The results in Tables 2-4 will be better a]]recoated of it is understtod that both the particular microbial species present in the reactors and their population are varying through the course of experimentation. With time the microorgansims adapt to the waste stream via natural selection, and the adaptation itself may depend, iter alia, on flow rate (LHSV). The p pulation mix and number means that a steady state may not have been achieved at all flow rates during the courses of experimentation. In fact, since low flow rates were chronologically the earliest experiments it is unlikely that a steady state was achieved at an LHSV of 0.03 hr -1 during the period of sampling. The chief consequence is that comparisons, even within the same reactor, of results at different LHSV are ambiguous.

TABLE 2

TABLE 2. Effluent Phenol Concentrations in Immobilized Whole Cell Reactors

LHSV,[a] hr^{-1}	Effluent Phenol Concentration ($\mu g/L$)			
	Reactor #1	Reactor #2	Reactor #3	Reactor #4
0.03	73 ± 31	72 ± 40	31 ± 21	31 ± 11
0.06	44 ± 9	45 ± 8	24 ± 12	29 ± 13
0.09	40 ± 16	33 ± 4	18 ± 6	b
0.12	23 ± 8	24 ± 3	12 ± 5	b

a. LHSV = liquid hourly space velocity. Hydraulic retention time (HRT) and LHSV are reciprocals, i.e., HRT = (1/LHSV)
b. Reactor #4 plugged

TABLE 3

TABLE 3. Effluent Suspended Solids in Immobilized Whole Cell Reactors

LHSV[a] hr^{-1}	Suspended Solids as O.D. 600 nm			
	Reactor #1	Reactor #2	Reactor #3	Reactor #4
0.03	0.190 ± 0.080	0.030 ± 0.015	0.046 ± 0.020	0.021 ± 0.010
0.06	0.102 ± 0.064	0.062 ± 0.012	0.029 ± 0.020	0.022 ± 0.020
0.09	0.064 ± 0.041	0.052 ± 0.041	0.040 ± 0.012	b
0.12	0.106 ± 0.091	0.048 ± 0.018	0.073 ± 0.034	b

a. LHSV = liquid hourly space velocity. Hydraulic retention time (HRT) and LHSV are reciprocals, i.e., HRT = (1/LHSV)
b. Reactor #4 plugged

Table 2 shows that at all HRT's the combination of foam having entrapped carbon andmicrooganisms afforded significantly lower phenol effluent levels than the other fixed bed reactors (#1 and #2), especially in achieving phenol effluent levels of 20 ppb and under. The data in Table 3 show that sludge formation, as measured by suspended soluids from our PBSS-packed reactors, was substantially less than that from prior art reactor #1, with reductions ranging from 32 to 76 percent. This comparison becomes even more favorable when it is realized that reactor #3 simultaneuously produces lower sludge formation and lower phenol effluent levels than does reactor #1.

TABLE 4

Effluent Phenol Levels from Immobilized Cell Reactors

DAYS	LHSV, hr^{-1}	EFFLUENT PHENOL CONCENTRATION (μg/L)			
		Reactor #1	Reactor #2	Reactor #3	Reactor #4
6	0.03	101	110	82	-
7	"	137	171	44	45
11	"	77	73	30	27
12	"	70	58	22	24
13	"	47	47	25	29
14	"	59	68	25	32
22	"	32	41	15	16
25	"	61	44	20	27
29	0.06	43	36	13	19
33	"	47	47	24	22
50	"	58	58	26	23
55	"	48	50	22	22
58	"	40	46	21	23
62	"	30	38	15	18
65	"	47	49	29	28
68	"	32	36	12	**
75	0.09	35	30	13	**
79	"	21	28	12	**
83	"	64	34	17	**
85	"	33	38	24	**
88	"	45	34	23	**
99	0.12	27	26	16	**
103	"	27	24	17	**
106	"	27	25	5	**
116	"	12	19	11	**

** - Reactor #4 plugged

The foregoing data show that tere is no significant difference between performance of the naturally immobilized cell reactor (i.e., where the cell are attached on the polypropylene surface) and cells immobilized in polypropylene surface) and cells immpbilized in polyurethane foam as regards effluent phenol levels, nevertheless there is lower sludge formation, as measured by lower suspended solids in the effluent, from the foam immobilized reactor compared to the biofilm reactor. However, the presence of activated carbon appears to have a significant and dramatic effect upon the level of phenol present in the reactor effluent, permitting phenol levels at or below 20 ppb.

EXAMPLE 8

Pilot Plant Operation. A scaled up version of reactors 3 and 4 of the foregoing example was used to process a slip stream of industrail wastewater at a coal tar processing plant. The reactor was 14 feet high with an inside diameter of 12.4 inches. Foam prepared as above but contianing approximately 33 weight percent powdered activated carbon was cut into cubes approximately 1 inch per side ans was used to pack the reactor along with air passed through a sparging tube. After an extensive shakedown period during which the effect of various independent variable supon system orperating performance was evaluated, the unit was operated at what was determined to be its optimum point forphenol removeal from the feedstock. This corresponded to a feed flow rate of 0.1 gallon per minute, or HRT of 15 hours, and an air flow of 1.15 SFCM.

The pilot plant was operated concurrently with a Leopold Upflow BioTower from Sybron Inc. which profcessed the industrial waste water from which the slip stream to the pilort plant was drawn. The

Bio-Tower was operated under conditions determined to be its optimum for phenol removal, which included an HRT of about 15 hours. The concurrent operation permitted a comparison of operational characteristics between the two units, some of which are summarized in the following tables.

The standard analytical test method for phenols using 4-aminoantipyrine (4-AAP) does not discriminate among individual phenolic components and also has been found to be subject to interference by many non-phenolic materials, such as aromatic hydrocarbons. In contrast, gas chromatographic analysis using a mass selective detector is both more sentsitive and discriminatory than the 4-AAP method, affording more reliable data.

TABLE 5

GC/MSD Analysis of Phenolics in Wastewater Feed and in Bio-Tower and Pilot Plant Effluents[a]

Sample No.	Component	Concentration (μg/L)		
		Wastewater	ICB Pilot Plant	Sybron Bio-Tower
1	phenol	393,000	14	11
	o-cresol	40,000	31	8
	m,p-cresol	62,000	7	28
	2,4-dimethyl phenol	6,000	9	36
	Phenolics by 4-AAP[b]	800,000	1,100	1,500
2	phenol	541,000	28	25
	o-cresol	42,000	31	201
	m,p-cresol	70,000	10	996
	2,4-dimethyl phenol	5,800	11	241
	Phenolics by 4-AAP	950,000	900	4,400
3	phenol	1,408,333	12	3,907
	2,4 dimethyl phenol	17,545	96	37
	TSS (mg/L)	59	208	1113
4	phenol	339,024	6	801
	2,4-dimethyl phenol	2,665	9	208
	TSS (mg/L)	55	189	760

a. GC/MSD stands for gas chromatographic analysis with mass selective detector.

b. 4-Aminoantipyrine analysis.

TABLE 6

Table 6 summarizes analytical results from a commercial environmental laboratory.

TABLE 6. Analytical Results from Independent Laboratory[a]

Pollutants	Feed[b]	Pilot Plant[b] Effluent	Bio-Tower[b] Effluent
2,4-DIMETHYLPHENOL	880	<100	130
PHENOL	240000	<100	<100
ACENAPHTHENE	620	<100	340
ACENAPHTHLENE	122	420	<100
FLUORANTHENE	130	<100	<100
NAPHTHALENE	5000	<100	260
PHENANTHRENE	350	<100	<100
	<400	<100	<100

a. Kemron Environmental Services, (109 Starlite Park, Marietta, Ohio 45715)

b. All units are micrograms per liter (μg/L). Detection Limits are: feed = 400; effluent = 100.

The foregoing data show that the method which is our invnetion is at least as efficent as a current commerical process, and is in fact even more efficient in removeal of some non-regulated phenolic materials such as the cresols and, especially, 2,4-dimethylphenol. In particular, it appears to more consistently reduce them to a level under the achieved by the comparison process. In addition, the ICB produced less than 25% of the sludge produced by the

comparison process.

The waste water also contained aromatic hydrocarbons as pollutants, and Table 7 shows that our method is as efficient as the ccommercial comparison process in the removal of these materials as well.

TABLE 7

Purge and Trap GC/FID Analysis of Benzene and Toluene.[a]

Run	Concentration (mass-ppb)					
	Influent Wastewater		Pilot Plant Effluent		Bio-Tower Effluent	
	Benzene	Toluene	Benzene	Toluene	Benzene	Toluene
1	3,800	2,400	25	10	35	10
2	6,200	4,100	35	14	26	8
3	4,800	1,600	12	6	–	–

a. GC/FID stands for gas chromatograph with flame ionization detector.

EXAMPLE 9

Laboratory Performance with Industrial Waste Water. A glass reactor as described in Example 7 used as a fixed bed the porous biomass system of Example 1 containing 33 weight percent powdered activated carbon. The microorganisms entrapped in the biofoam were enrichement cultures drom the wastewater and soil at the site prepared as described in Example 6. The reactors (ICB) were operated at a hydraulic retention time of 24 hours using a sample of industrial waste water from a phenol production plant. For comparison, effluent of the same waste water treated with activated sludege for 120 hours is also shown. Table 8 shows that both benzene and pheol are degreaded almost completely immediately upon operation of the unit. A second trial afforded similar results. Table

9 shows the effect of hydraulic retention time on phenol breakthrough, and shows similar phenol degradation at hydraulic retention times as low as about 8 hours. As previously noted the penolic assay by 4-aminoantipyrine is subject to interfacence by a nyriad of substances, including aromatic hydrocarbons, which are likely to be found in the waste waters. Therefore the results of they analysis in this table are to be used solely to indicate a ttrend rather than for absolute purposes. In contrast, Table 10 affords an analytical result as obtained via GC/MSD analysis in which the effect of interfering substances has been removed and which gives much more reliable analysis then the 4-AAP method. Among other things, Tab;e 10 shows the normous reduction in sludge production by the methood of this invention relative to that of a typical retention basin Finally, Table 11 shows more complete analytical data for effluent, from which it can be concluded that our reactor affords more complete degradation of most organic pollutants in 24 hours than does activated sludge in a retentikon basin in 120 hours.

TABLE 8

Immobilized Whole Cell Reactor Treatment of an Industrial Waste VT-633. Additional Phenol and Benzene Added.

Time (hours)[d]	23.8	30.3	47.3
Influent Benzene Conc. (ppb)	2644.0	3200.0	920.0
Incremental Total Benzene Loaded (μg)	621.3	294.4	220.8
Incremental Total Effluent Benzene (μg)[b]	< 0.5	< 0.2	< 0.5
Total Trapped Benzene in air (μg)	3.0	0.8	1.7
% Benzene Degraded	> 99.4	> 99.7	> 99.0
Influent Phenolics Conc. (ppm)[a]	141.6	144.8	135.3
Effluent Phenol Conc. (ppm)[b]	bmdl[c]	bmdl[c]	bmdl[c]
% Phenol Degraded	> 99.5	> 99.5	> 99.5

a. Total phenolics by 4-AAP assay.

b. Minimum detection limits: phenol .2 ppm by 4-AAP assay; benzene, 2 parts per billion by purge and trap gas chromatography with flame ionization detector.

c. bmdl = below minimum detection limit.

d. Time from startup.

TABLE 9

Immobilized Whole Cell Reactor Treatment of an Industrial Waste VT-633.

Accumulative Time (hrs):	26.25	52.25	77.25	105.25	123.75	150.08	173.08	198.08	224.08
Lapsed Time (hrs):	26.25	26.00	25.00	28.00	18.50	26.33	23.00	25.00	26.00
HRT (hr/col):	23.3	25.4	23.3	11.0	11.0	10.6	8.7	8.6	7.2
Influent Total Phenolics Conc.(ppm):	64.7	43.0	45.9	45.7	45.2	45.5	45.7	50.6	54.7
Effluent Phenol Conc.(ppm):	2.0	3.5	3.7	3.6	4.8	3.8	3.6	3.7	6.3
% Phenol Degraded:	97.0	91.9	91.9	92.1	91.2	91.6	92.1	92.7	88.5

TABLE 10

Analysis of Untreated, ICB Treated and Activated Sludge Treated Wastewater

Component	Concentration (ppb)		
	Untreated	ICB	Activated Sludge
Acetone	1,350,000	100,000	850,000
Phenol	35,000	10	10
Benzene	350	20	20

ICB
- 24 hr retention time
- 0.58 mg. sludge/liter effluent

Activated Sludge
- 120 hr. retention time
- 1.75 mg sludge/liter effluent

TABLE 11. Water Analyses Results, ppb

Compound	ICB Reactor	Active Sludge
Acetone	100,000	850,000
Benzene	20	20
Butanone	<10	200
Pentanone	<10	300
Chloroform	300	200
Epoxy ketone	600	3000
Diacetone alcohol	350	1700
C_9 ketone?	2000	4000
Methyl cyclohexenone	700	3500
Dimethyl phenyl carbinol	60,000	200,000
Acetophenone	<10	10,000
Acetyl cyclohexanone	300	3500
Unknown M. W. 126	100	75
Phenol	10	10

EXAMPLE 10

Comparison of Reactor Configuratikon on Sludge Production. A model wastewater feed (described in Example 7) was treated in three bench scale reactors. Two were 500 ml New Brunswich glass fermenters that were continuously mixed with a mechanical stirrer. One of these fermentors were continuously mixed with a mechanical stirrer. One of these fermentros were operated as a chemostat in which the wastewater was pumped through with ahydraulic retentikon time of 33 hours. In this reactor in the effluent. A second mixed reactor was filled with approximately 200 ml of biofoam and operated similarly. The third reactor consisted of a 500 mil ICB bench scale reactor, as described in Example 1, using as a fixed bed the same biofoam as used in the foregoing second mixed reactor. This reactor was operated with a hydraulic retention time of 12.5 hours. The ICB reactor produced both lower sludge and better phenol removal efficiency then either of the mixed reactors, as shown in Table 12.

Table 12. Sludge Formation in Various Reactors

Reactor	HRT (hrs)	Effluent Phenol[c] (µg/L)	Sludge[c]	
			OD 600 nm[a]	TSS (mg/L)[b]
Continuous Stirred Tank Reactor (CSTR)	33	820	0.45	680
CSTR + Biofoam	33	62	0.36	606
ICB	13	19	0.07	96

a. Sludge as measured by turbidity; optional density at 600 nm.
b. Total suspended solids.
c. Measurements taken after 1 void volume for the CSTR reactors, and after 33 hours for the ICB. None represent steady state conditions.

These data clearly and unambiguously show a substantial, quite significant reduction in sludge production using our biofoam in a fixed bed reactor.

WHAT IS CLAIMED IS

1. A biomass support system comprising a hydrophilic polyurethane foam and activated carbon.

2. The support system of claim 1 wherein hydrophilic polyurethane foam is prepared from a polyisocyanate compound and a polyol wherein at least 80% by weight of the polyol content is polyethylene oxide.

3. The support system of claim 2 wherein the polyol is at least 90% by weight polyethylene oxide.

4. The support system of claim 3 wherein the polyol content is greater than about 99% by weight polyethylene axide.

5. The support system of claim 2 wherein the polyisocyanate component contains from about 1 to less than about 25% by weight aromatic isocyanate.

6. The support system of claim 3 wherein the aromatic isocyanate content ranges from about 1 to less 20% by weight.

7. The support system of claim 4 wherein the aromatic isocyanate content ranges from about 1 to less than about 15% by weight.

8. The support system of claim 1 wherein said activated carbon is selected from wood charcoal and anthracite coal.

9. The support system of claim 8 wherein the activated carbon is wood charcoal.

10. The support system of claim 1 wherein said activated charcoal has a K_d value ranging from about 0.001 mg/L to about 300 mg/L.

11. A porous biomass support comprising (i) a hydrophilic polyurethane foam, (ii) activated carbon and (iii) a phenolic degrading microorganisms; said activated carbon and microorganisms having K_d and K_s values in order that the K_s/K_d ratio is between about 1:1 and about 1:50.

12. A method for the aerobic biodegration of phenolic materials in aqueous streams to a level under 0.1 parts per million in a period of no more than 30 hours comprising flowing an aqueous materials in the presence of oxygen through a fixed mass of the porous biomass support system of claim 1.

Figure 1. Adsorption Curves for Foams and Carbon Impregnated Foams

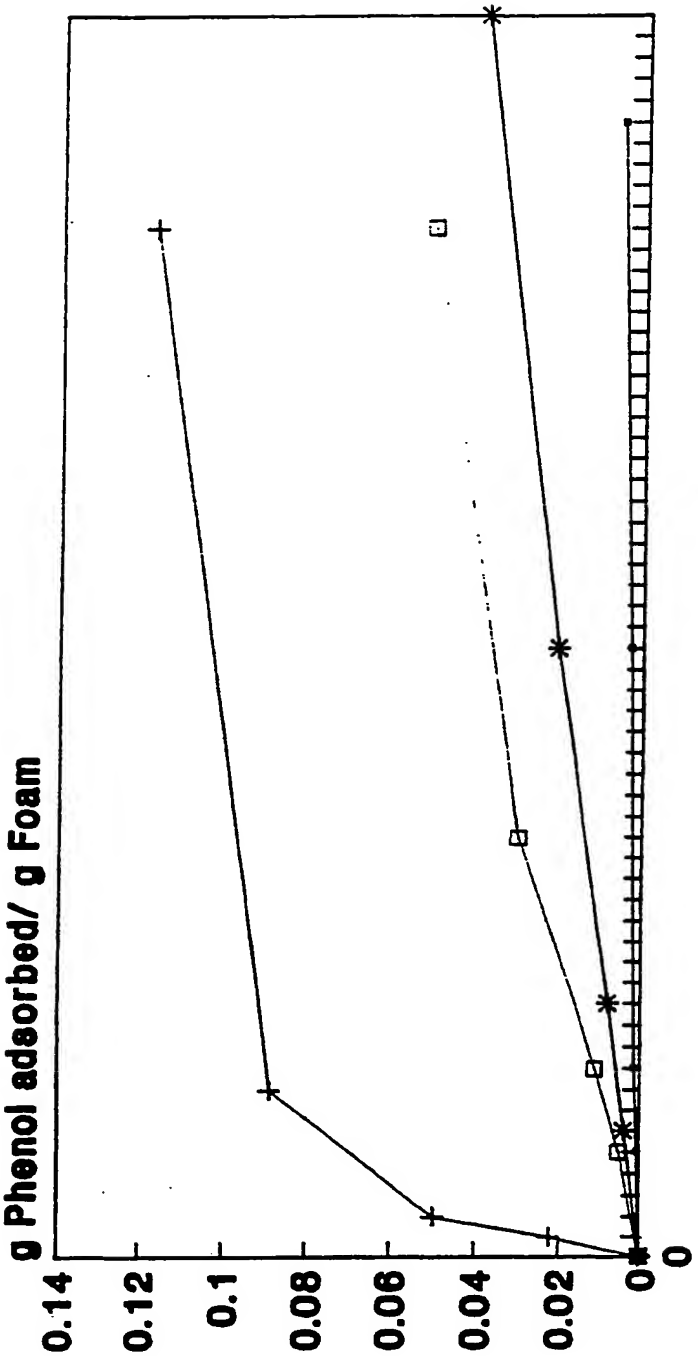


Figure 2. Adsorption Curves for Hydrophilic Foam & Carbon Impregnated Foam

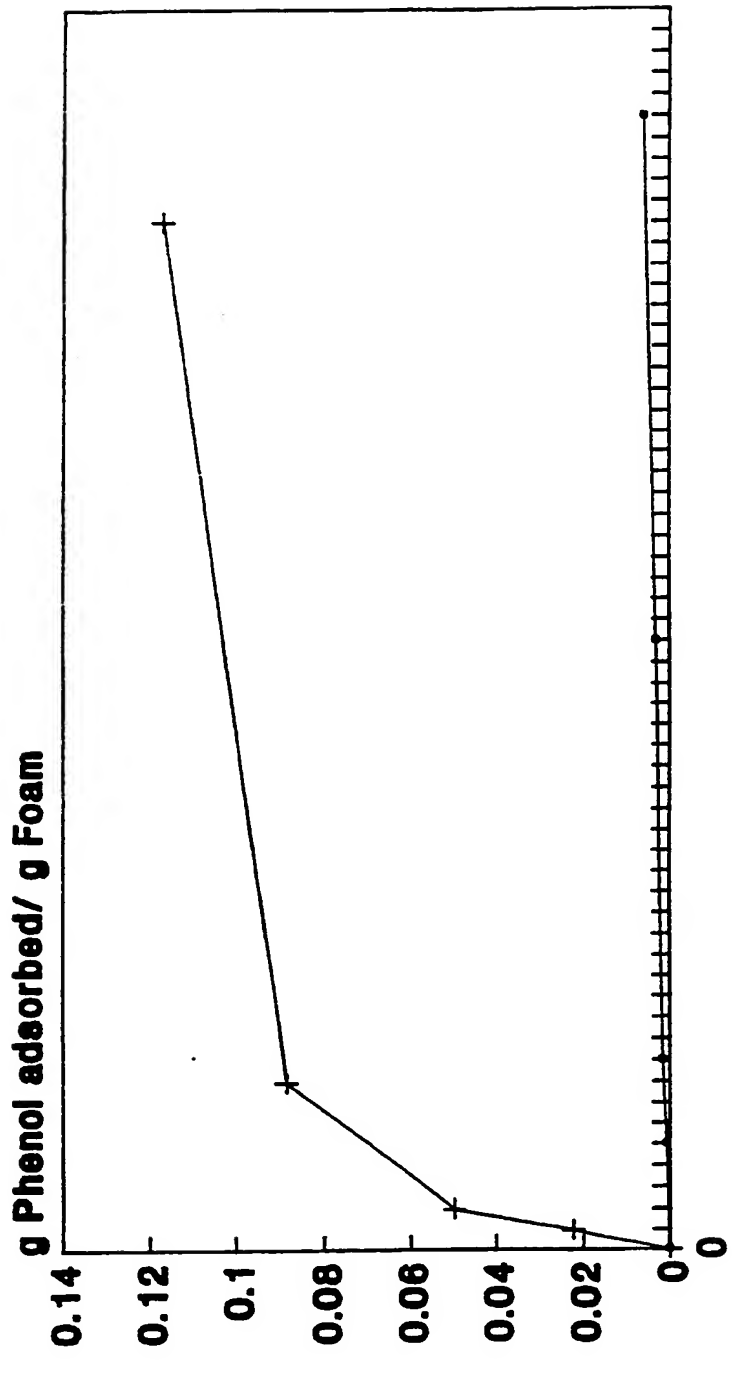


Figure 3. Adsorption Curves for Hydrophobic Foam and Carbon Impregnated Foam

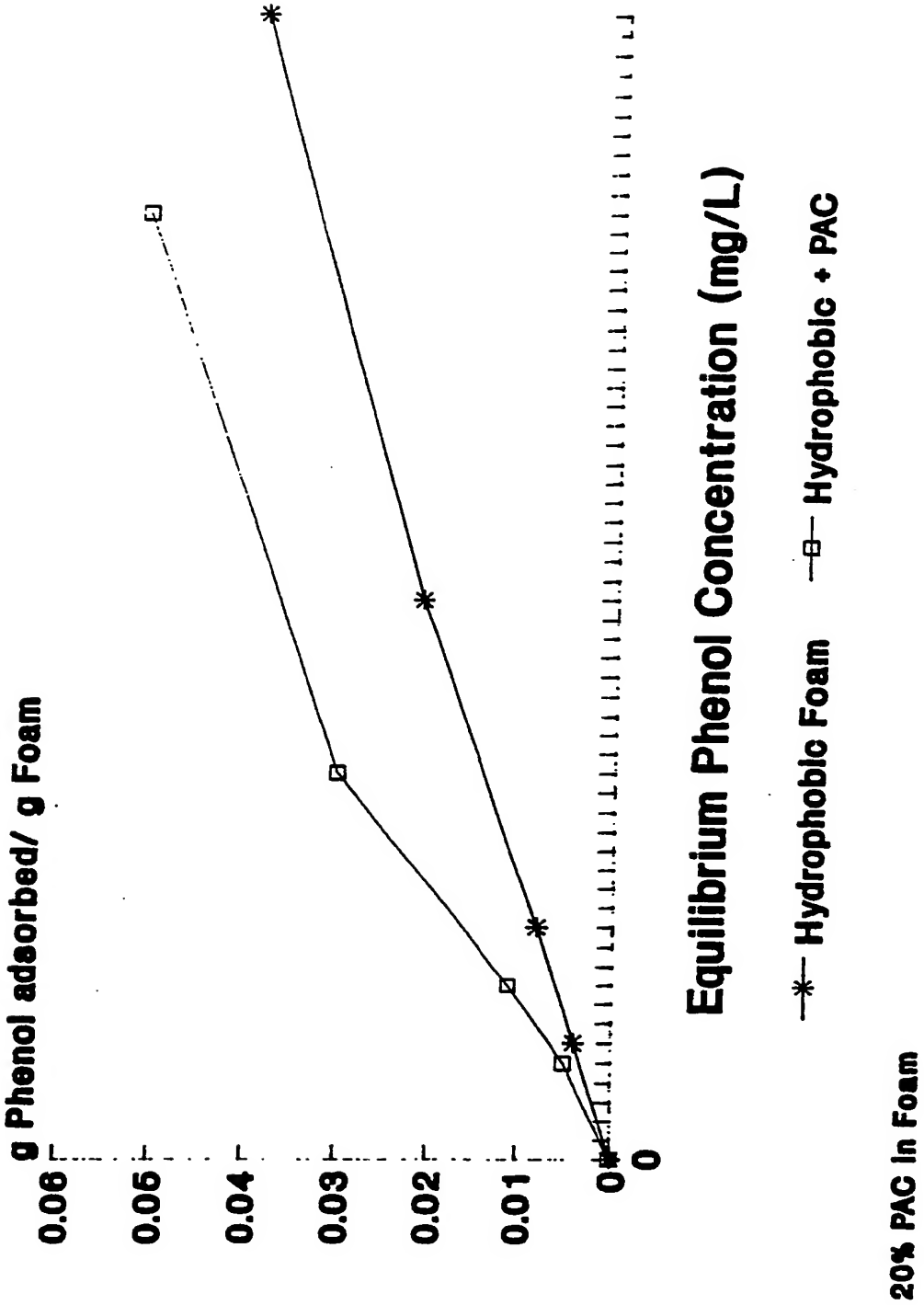


Figure 4

FIGURE 4a. 1-PULSE C-13-NMR OF ICB SYSTEM (All phenol – includes both mobile and solid or tightly bound phenol).

FIGURE 4b. CPMAS C-13 NMR OF ICB SYSTEM (Solid or tightly bound phenol only).

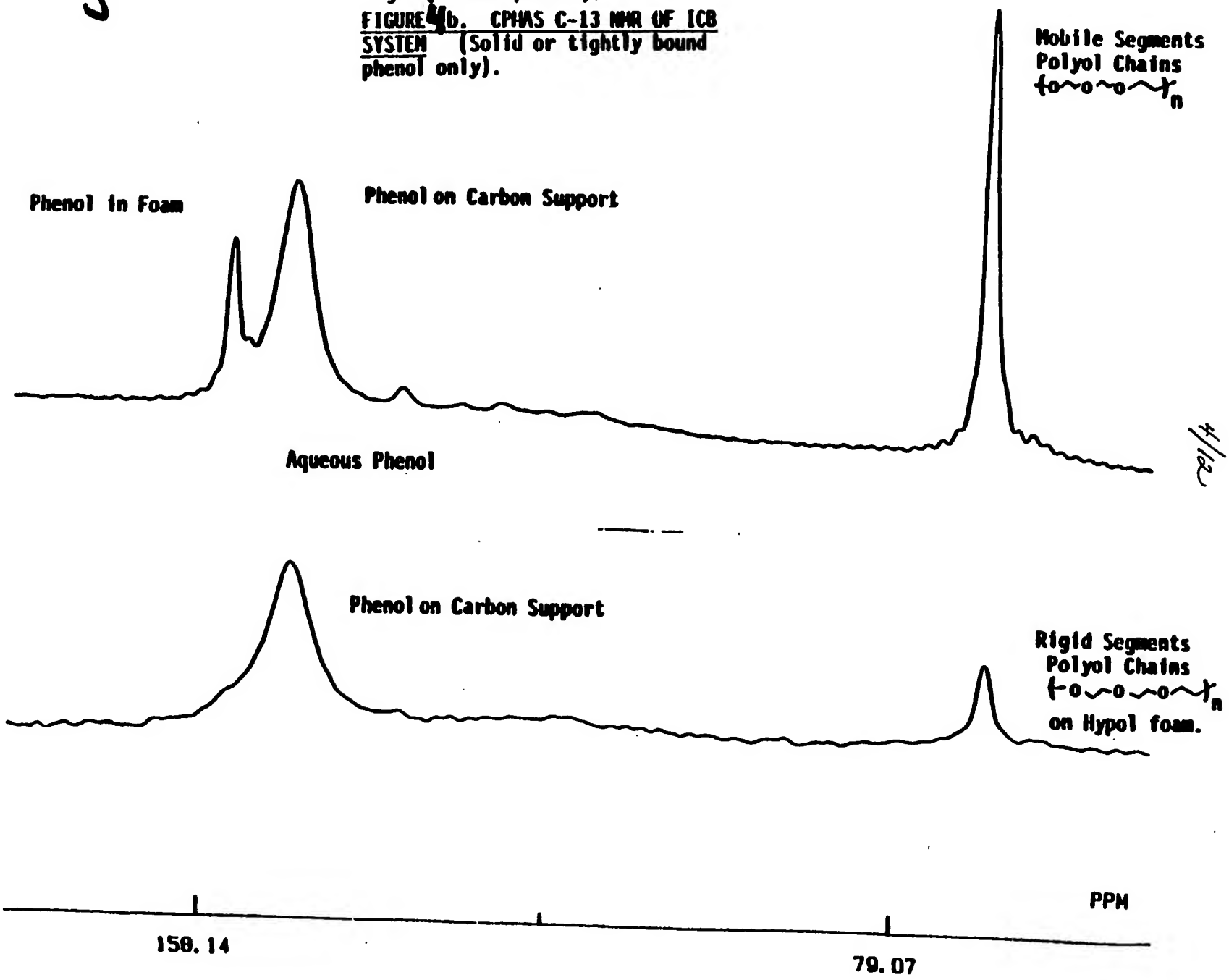
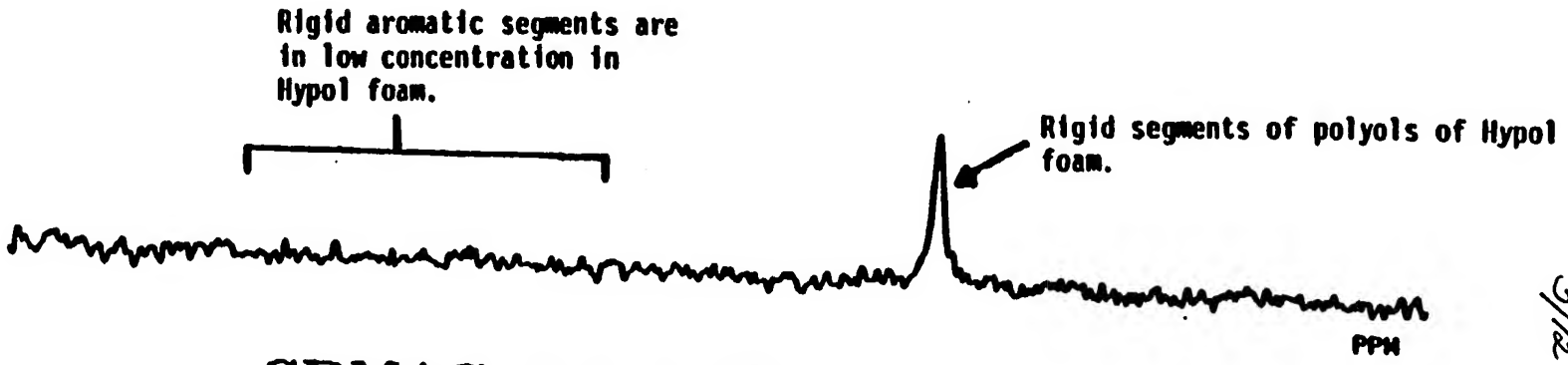


Figure 5

FIGURE 5a. CPMAS C-13 NMR OF HYPOL FOAM.

FIGURE 5b. CPMAS C-13 NMR OF GENERAL FOAM.

CPMAS OF HYPOL FOAM



CPMAS OF GENERAL FOAM

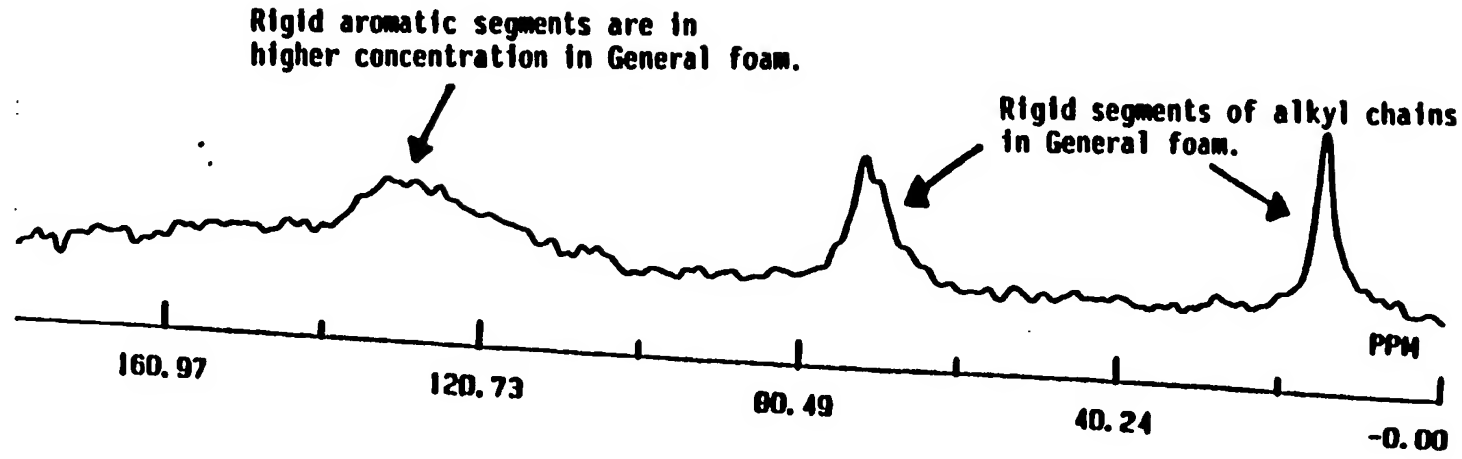
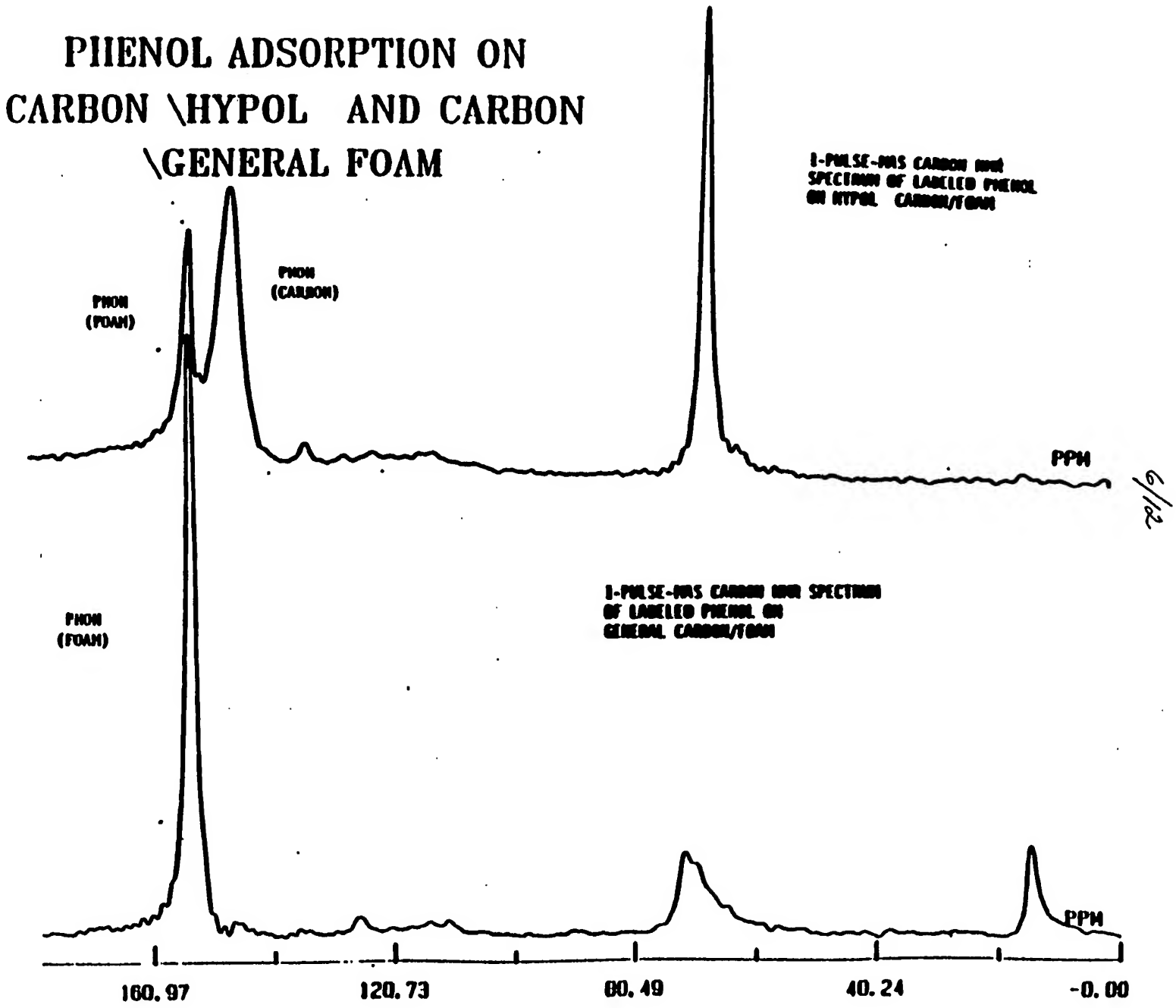
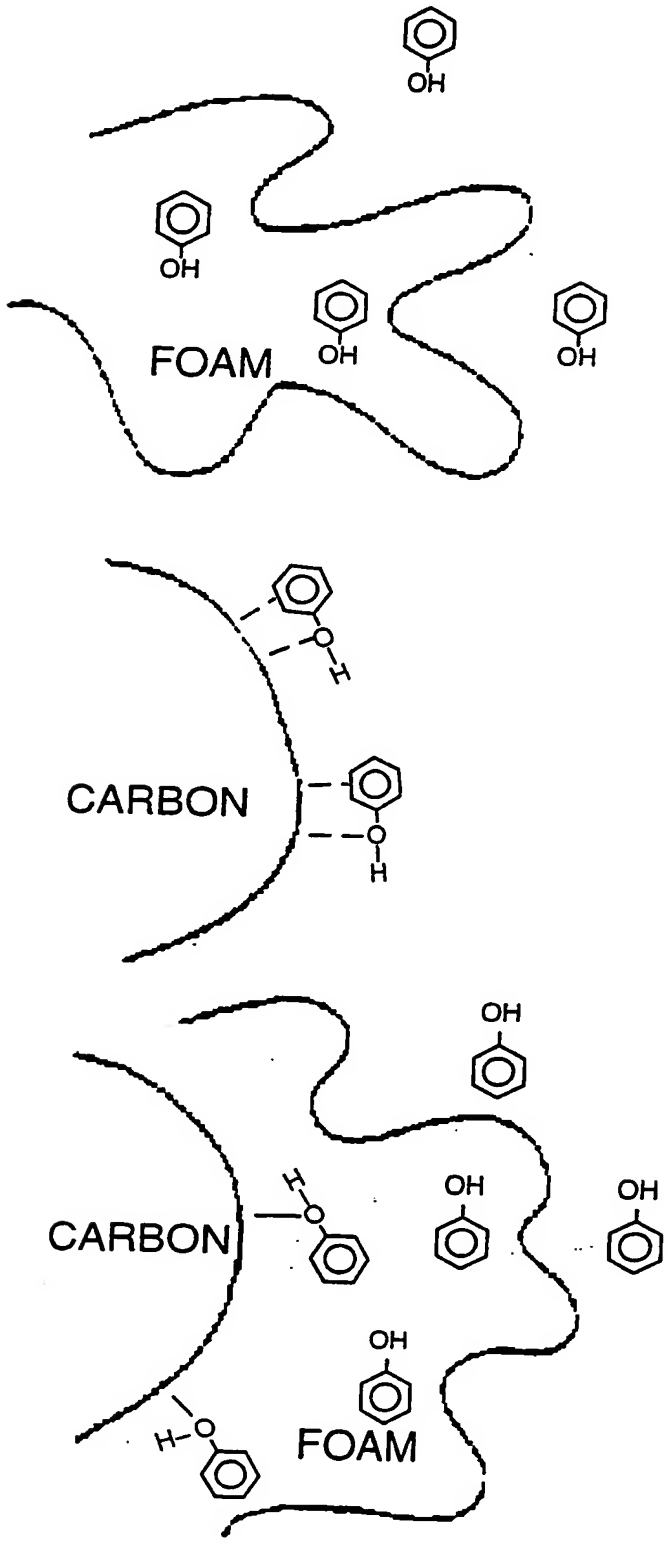


FIGURE 6


PHENOL ADSORPTION ON CARBON \HYPOL AND CARBON \GENERAL FOAM
PHOH (FOAM)
PHOH (CARBON)
PPM
PHOH (FOAM)
PPM
160.97
120.73
80.49
40.24
-0.00

7/12

Figure 7
Summary From C-13 NMR Results



8/12

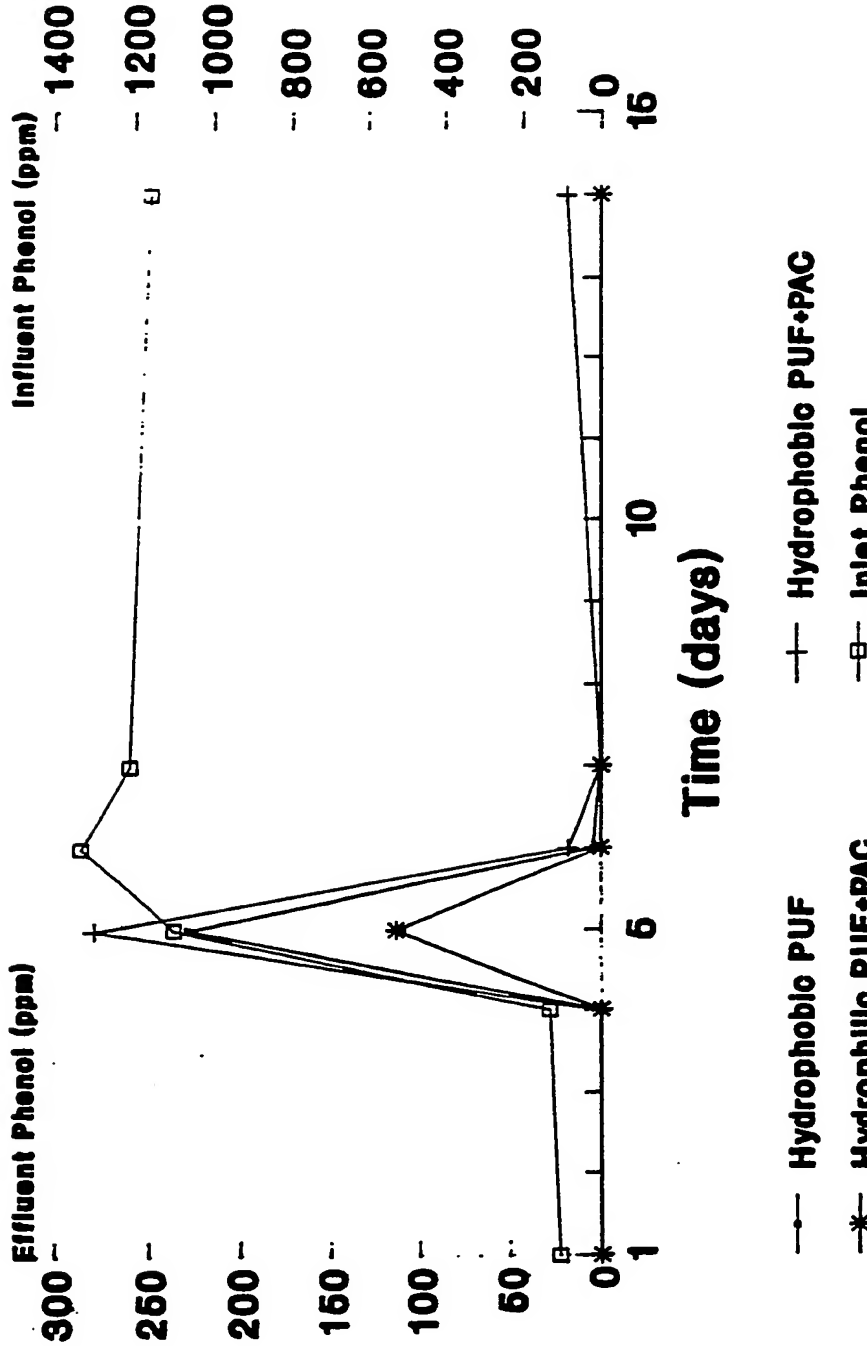


Figure 8. Response of Bioreactors Containing PUF Supports to Shock Loads of Phenol

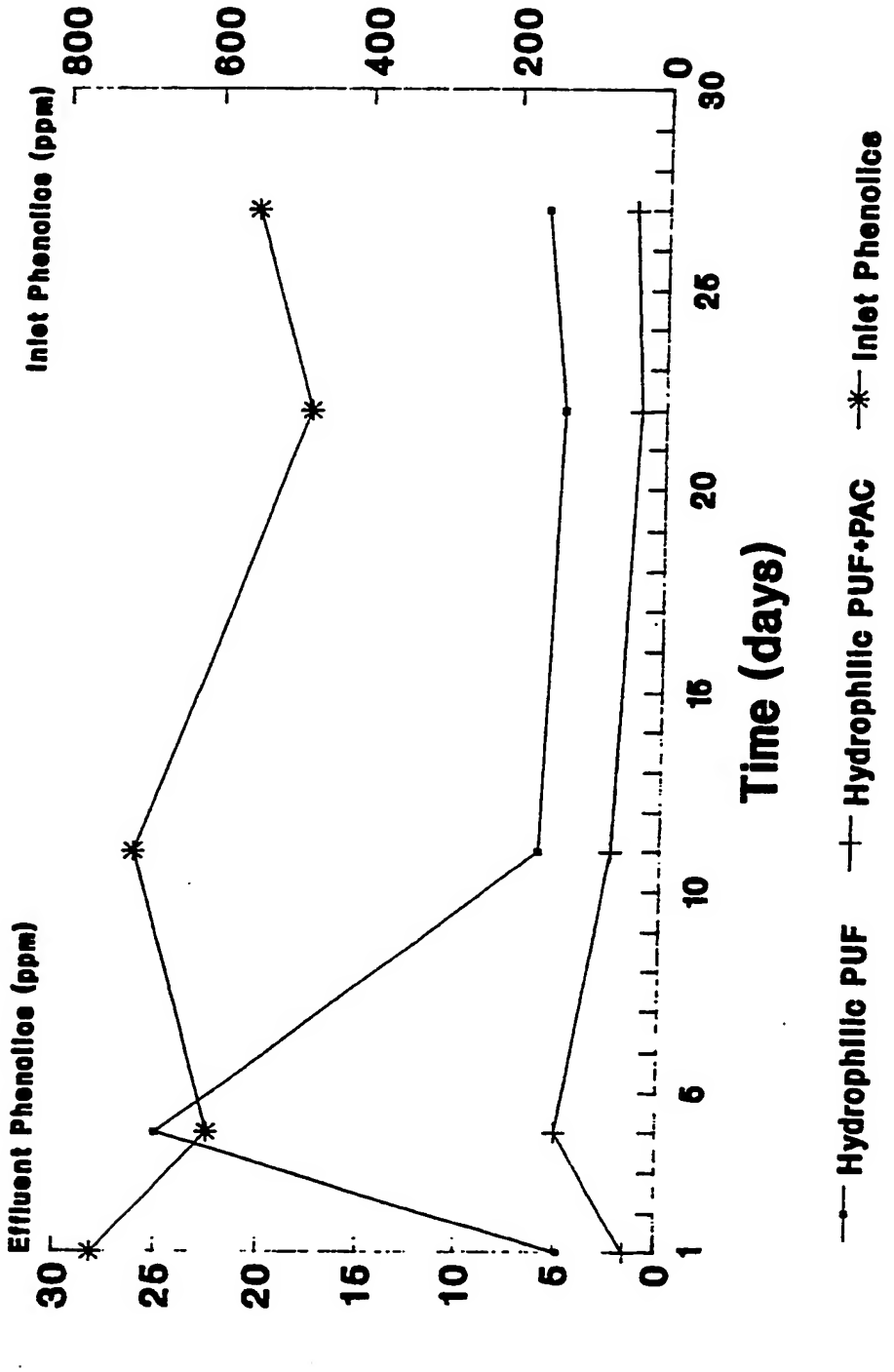


Figure 9. Total Phenolics Removal by Bioreactors using Polyurethane Foam Supports

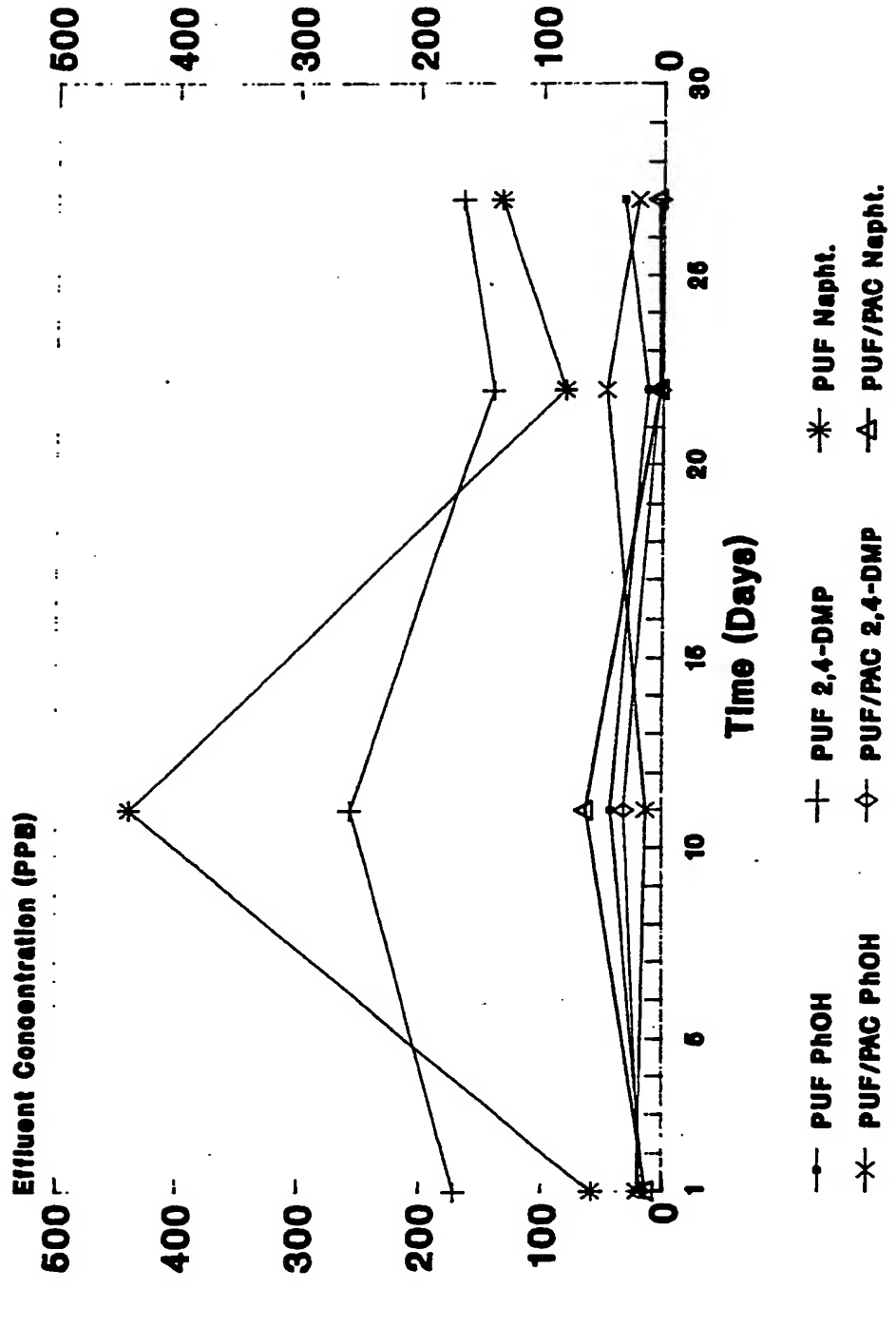


Figure 10. Aromatic Pollutant Removal by Reactors Using Polyurethane Foam Supports

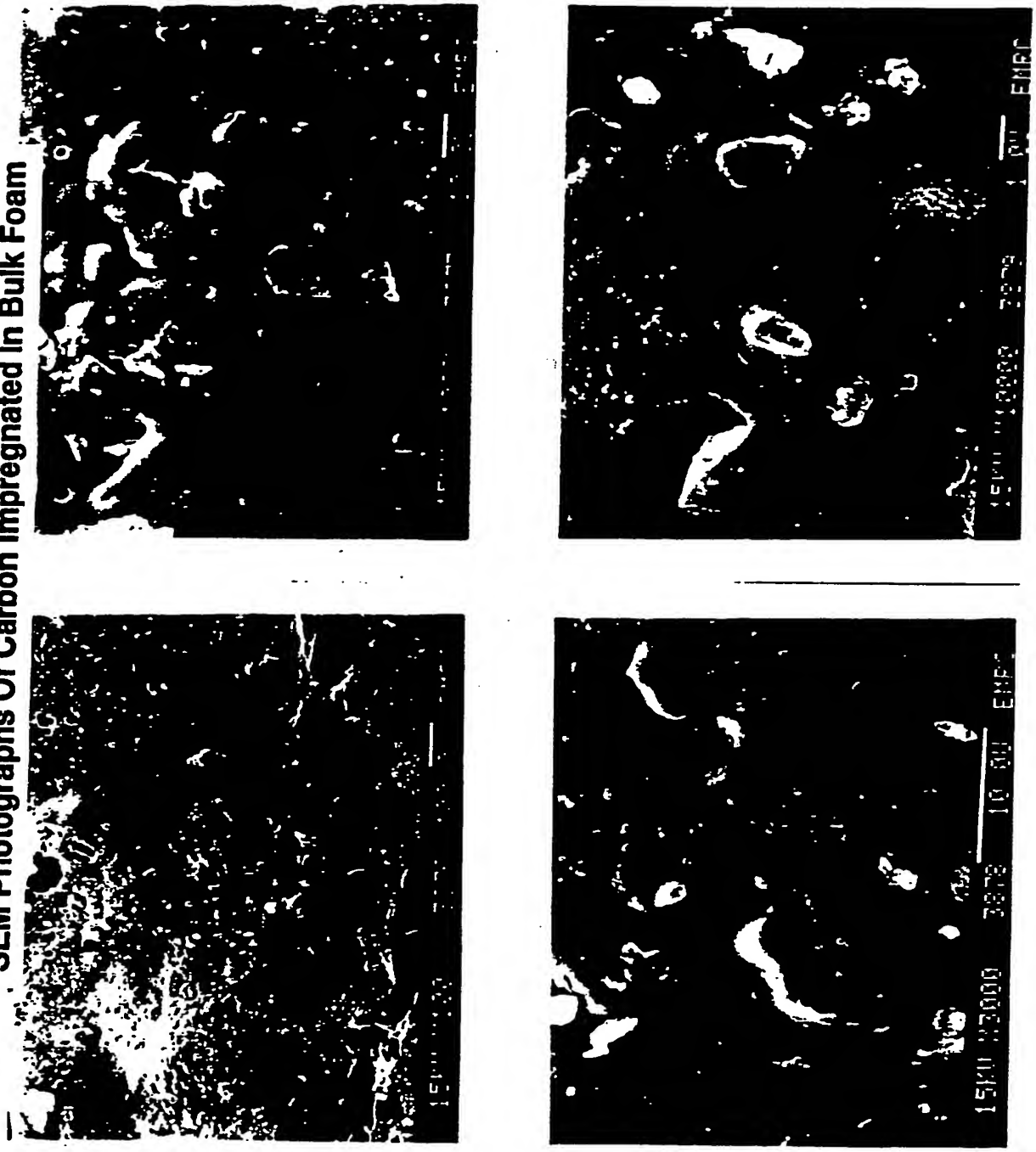


Figure 11
SEM Photographs Of Carbon Impregnated In Bulk Foam

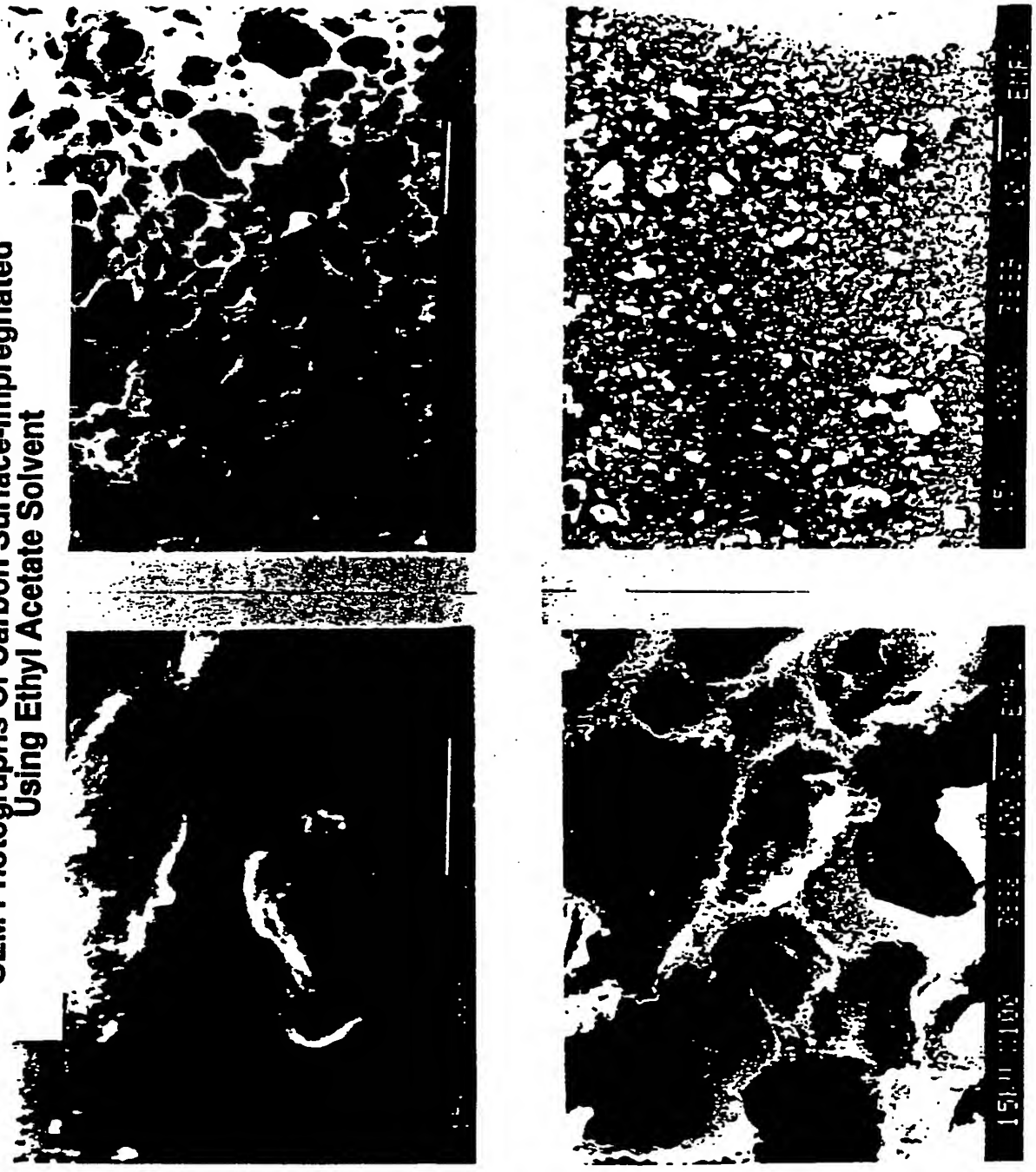


Figure 12
SEM Photographs Of Carbon Surface-Impregnated Using Ethyl Acetate Solvent

INTERNATIONAL SEARCH REPORT

PCT/US 91/07436

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C02F3/10; C08G18/48

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C02F ; C08G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 150 747 (BAYER) 7 August 1985 see page 79; claim 1 see page 23, line 12 - line 26 see page 24, line 23 - page 25, line 7 see page 33, line 11 - line 25 see page 43 - page 46, line 3 see page 64; example 7	1,5,6,8
A		2-4,11, 12

P,X	WO,A,9 011 970 (ALLIED-SIGNAL INC.) 18 October 1990 cited in the application see page 56; claims 1,6 see page 20, line 13 - page 21, line 17 see page 25, line 28 - page 26, line 31 see page 28, line 35 - page 29, line 21	1,8,12
A		2-7,11

	-/--	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 MARCH 1992	11. 03. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	TEPLY J.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 781 231 (MINNESOTA MINING AND MANUFACTURING COMPANY) 25 December 1973 see column 8; claims 1,2 see column 6, line 10 - line 20 ---	1-4

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9107436 SA 53794

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 03/03/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0150747	07-08-85	DE-A- 3402697	01-08-85
		CA-A- 1249674	31-01-89
		JP-A- 60172399	05-09-85
		US-A- 4576718	18-03-86
WO-A-9011970	18-10-90	US-A- 4983299	08-01-91
		CA-A- 2014030	10-10-90
		EP-A- 0467969	29-01-92
US-A-3781231	25-12-73	None	